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LLNL SFA FY11 Program Management and Performance Report: Environmental Transport of Plutonium

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LLNL SFA FY11 Program Management and Performance Report:

Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

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1. Program Overview

The major challenge in predicting the mobility and transport of plutonium (Pu) is determining the dominant geochemical processes that control its behavior in the subsurface. The reaction chemistry of Pu (*i.e.*, aqueous speciation, solubility, sorptivity, redox chemistry, and affinity for colloidal particles, both abiotic and microbially mediated) is particularly complicated. It is generally thought that due to its low solubility and high sorptivity, Pu migration in the environment occurs only when facilitated by transport on particulate matter (*i.e.*, colloidal particles). Despite the recognized importance of colloid-facilitated transport of Pu, very little is known about the geochemical and biochemical mechanisms controlling Pu-colloid formation and association, particularly at femtomolar Pu concentrations observed at DOE sites.

Reactive transport models that address geochemical processes occurring at the mineral-water interface are still in their infancy for multi-phase systems (U.S. DEPARTMENT OF ENERGY, 2007). Generally, existing transport models have ignored the coupled factors of redox chemistry and microbial activity and have relied on empirical equilibrium or rate-limited distribution coefficient (K_d) models to address actinide retardation and colloid-facilitated transport (*e.g.*, Glynn, 2003; Pickett, 2005; Tien and Jen, 2007). Recent experimental data from Powell and others (Kaplan et al., 2004; Powell et al., 2005; Kaplan et al., 2006; Demirkanli et al., 2008) that these simplified models cannot adequately predict Pu transport because they do not capture the coupled processes controlling Pu sorption and desorption.

This 5-year program is designed to test the important biogeochemical processes governing colloid-facilitated Pu transport in the field. We hypothesize that biogeochemical processes operating under low (10^{-9} – 10^{-16} mol/L), environmentally relevant, concentrations are fundamentally different from those operating in simple, binary-system laboratory experiments conducted at high Pu concentrations (10^{-4} – 10^{-9} mol/L). At environmentally relevant concentrations, Pu will be controlled by one or more of the following processes:

- binary sorption to low-site-density, high-affinity colloid surface sites (*e.g.*, surface defects),
- stabilization of Pu surface complexes on mineral colloids by natural organic matter coatings,
- surface precipitation of Pu polymers: experimental and natural nano-colloids,
- co-precipitation with colloids as a result of mineral alteration, and
- direct and indirect microbial interactions with Pu and colloids.

Our hypothesis is being tested by selectively examining each process separately as a function of concentration and then evaluating its potential role in Pu transport. Laboratory results are being compared to field samples taken from contaminated sites (NTS, RFETS, the Hanford Reservation and Tomsk, Russia) where Pu-containing colloids/particles will be and characterized. The processes listed above form the basis for 5 Program Elements, each with its own hypothesis-driven research program. However, each Program Element includes tasks that integrate aspects of this research plan to address our central hypothesis. Program Elements include computational chemistry studies, controlled laboratory experiments, geochemical modeling, and field sample characterization efforts that address length scales from the atomic to the field scale.

2. Scientific Objectives

The objective of this science program is the identification and quantification of the biogeochemical processes that control the fate and transport of Pu at picomolar to attomolar (10^{-12} – 10^{-18} mol/L) concentrations. We are investigating the roles of mineral surface defects, ternary complexes, polymerization, co-precipitation/surface alteration, as well as direct and indirect microbial interactions on the affinity and sorption/desorption rates of Pu. With the use of unique state-of-the-art facilities at LLNL such as the accelerator mass spectrometer (AMS), a NuPlasma HR IsoProbe mass spectrometer (MC-ICPMS), the Transmission Electron Microscope (TEM), and the nano-secondary ion mass spectrometer (NanoSIMS), we are conducting laboratory experiments on colloids at environmentally relevant concentrations. A primary goal of this program is to provide the DOE with the scientific basis to support decisions for the remediation and long-term stewardship of legacy sites.

3. Program Structure

Dr. Kersting is the program manager and point of contact for this program. She is also Director of the LLNL branch of the Glenn T. Seaborg Institute (Seaborg Institute) and reports directly to the Associate Director of the Physical & Life Sciences (PLS) Directorate, Bill Goldstein. Henry Shaw is the point-of-contact for LLNL's, BER Programs and is the Chief Scientist for PLS reporting directly to Bill Goldstein. This SFA program is managed through the Seaborg Institute and is aligned with the Seaborg Institute's research focus on environmental radiochemistry, nuclear forensics and super heavy element discovery.

Dr. Kersting communicates BER program needs to both the Lead Scientist, Dr. Zavarin, and Program Element leads, coordinates program execution, insures financial responsibility in spending, planning, and program direction. Monthly program meetings/teleconferences with all staff members leads will serve to communicate progress and ensure that the program goals are being met. Each Program Element has a lead scientist that reports to both the SFA manager (Dr. Kersting) and lead scientist (Dr. Zavarin). Dr. Kersting reports to both LLNL senior management and BER (Arthur Katz). Dr. Zavarin ensures that Program Element efforts at LLNL and collaborating institutions are aligned with the research outlined.

The majority of the experimental work (Program Elements A, C, and D) is led by LLNL scientists under the supervision of Dr. Zavarin in his environmental radiochemistry laboratories. Program Element B and E leads and their post-docs/graduate students have access to LLNL through the Laboratory's Visiting Scientist Program. The sorption/desorption experiments in Program Element B (B. Powell lead) is a coordinated effort between Clemson University and LLNL. The microbial work in Program Element E (D. Moser lead) is carried out at the Desert Research Institute and LLNL. Characterization and isolation of microbial populations in Pu-contaminated groundwater at the NTS are coordinated through external programs (*e.g.*, UGTA). Groundwater and sediment sample collection at other field sites is being coordinated through targeted collaborations (Hanford (A. Felmy); Tomsk, Russia (S. Kalmykov)).

In addition to the roles of Dr. Kersting and Dr. Zavarin discussed above, each team member is indentified below.

Annie Kersting—Director of the Glenn T. Seaborg Institute at LLNL, which conducts research on environmental radiochemistry and nuclear forensics. She also oversees both the postdoc (~90 postdocs) and a nuclear forensics summer student program (~10- summer students). Her research focuses on actinide transport in the subsurface. Dr. Kersting is the program manager for this SFA and is the lead on Program Element C: Surface precipitation of Pu polymers and field samples. She co-supervises postdocs Ruth Tinnacher, Ruth Kips and James Begg (FY10 new hire), and coordinates summer students.

Mavrik Zavarin—LLNL Project manager for the Underground Test Area (UGTA) program responsible for identifying the extent of radiologic contamination at the NTS. Dr. Zavarin has been involved in experimental and modeling studies of radionuclide chemistry at the mineral-water interface, mineral dissolution/precipitation kinetics, colloid-facilitated transport, and radionuclide reactive transport modeling. Dr. Zavarin is the Lead Scientist, is responsible overseeing Program Elements A-E and also the lead for Program Element A: Binary sorption to low-density high affinity surface sites. Dr. Zavarin coordinates NTS field operations with UGTA for program Element E: microbial interactions. He co-supervises postdocs Ruth Tinnacher, and James Begg (FY10 new hire).

Brian Powell—Assistant professor, Clemson University, radiochemist. Prof. Powell's research focuses on understanding and quantifying the rates and mechanisms of actinide interactions with natural soils and synthetic minerals. He continues to be involved with experimental and modeling studies of long-term Pu vadose zone transport at the Savannah River Site. Prof. Powell will coordinate activities between Clemson and LLNL and supervises graduate students that carry out graduate thesis work on this project.

Duane Moser—Microbial Ecologist at the Desert Research Institute. Dr. Moser has over 15 years of experience in monitoring microorganisms and their activities in the environment with an emphasis on the deep subsurface, aquatic systems and bioremediation. Moser is experienced in molecular- and cultivation-based approaches for microbial detection and provides a full complement of microbiological tools and analyses for the team, both field and laboratory. He supervises postdoc, Jen Fisher.

Pihong Zhao Radiochemist with over 16 years experience in environmental radiochemistry, waste form, thermodynamic data measurements for actinides and development of actinides separations. Dr. Zhao serves as lab manager for the program and has daily oversight responsibility over post-doc and student laboratory activities as part of this SFA.

Robert Maxwell—Chemist with expertise application of nuclear magnetic resonance methods to the study of the structure and dynamics of materials, polymer aging and degradation, dissolution kinetics of silica polymorphs, and organic-inorganic composite materials.

Susan Carroll—Geochemist who has conducted and published research for a variety of rock-water systems focusing on experimental surface chemistry, mineral kinetics, mobility of metal and radioactive contaminants, and geologic CO₂ sequestration. She supervises postdoc Harris Mason.

Zurong Dai—Physicist, materials scientist at LLNL. Dr. Dai has more than 20 years experience in structural characterization of natural and man-made materials by using TEM. His research focuses on crystal growth and crystallography, nano-materials synthesis and characterization, experimental measurement of electronic structure and optical properties of materials. Dr. Dai will be responsible for the TEM analyses.

Ross Williams—Isotope geochemist at LLNL, Dr. Williams is the laboratory manager for the Chemical Science Division's ICP-MS Facility and chief scientists for the multi-collector NuPlasma HR IsoProbe ICPMS. Dr. Williams sets the standard for isotope ratio mass spectrometry in the DOE complex. He has more than 20 years of experience in actinide radiochemistry and metrology. Dr. Williams will be responsible for measurement and interpretation of ICP-MS measurements.

Scott Tumey—Radioanalytical chemist at the LLNL Center for Accelerator Mass Spectrometry (CAMS). Dr. Tumey is a key member of the heavy-isotope group at CAMS and has played a central role in developing AMS measurement capabilities for actinides. Dr. Tumey will oversee the preparation and measurement of samples by AMS, and helps design laboratory experiments so that they adequately reflect the sample requirements of AMS.

Ruth Tinnacher—Postdoctoral fellow at LLNL. Dr. Tinnacher's research focuses on parameters and processes that control the sorption, remobilization and transport behavior of actinides in the environment such as organic and inorganic colloids and metal sorption/desorption kinetics. She has several years of experience in conducting lab-scale experiments with uranium, Pu and various organic matter fractions using batch, static column and advective column systems. Dr. Tinnacher will conduct sorption/desorption experiments.

Ruth Kips—Postdoctoral fellow at LLNL. Dr. Kips' research focuses on nuclear safeguards and the application of micro-analytical tools to the analysis of sub-micrometer-sized actinide particles to determine their morphological, isotopic, and compositional characteristics using electron microscopy, X-ray diffraction, ICP-MS, and NanoSIMS. She will use the NanoSIMS to characterize field and experimentally derived colloids.

Harris Mason—Postdoctoral fellow at LLNL. Dr. Mason's research focuses on applying NMR spectroscopic techniques to investigate metal sorption reactions at the mineral/water interface. He will use these methods to investigate how Pu behaves at the silica interface.

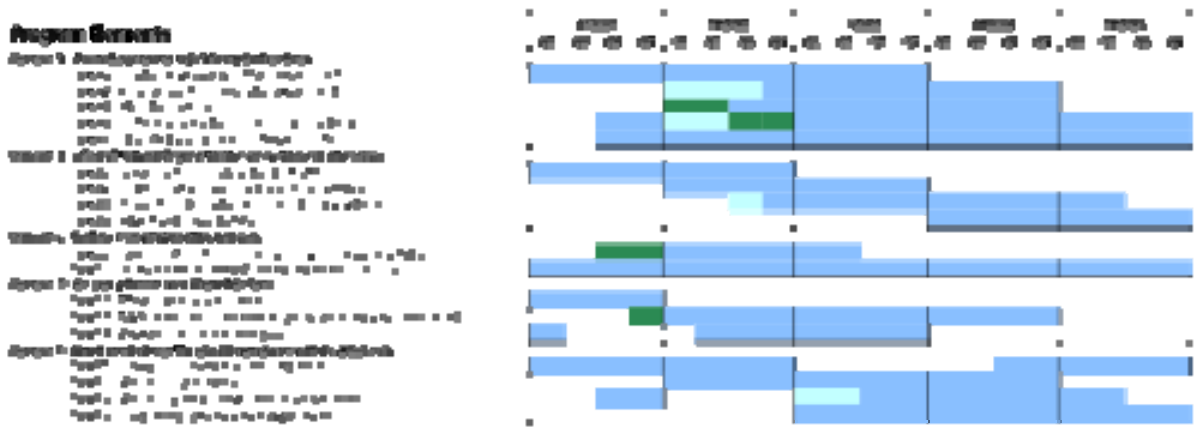
Jen Fisher— Postdoctoral associate at the Desert Research Institute. Dr. Fisher's research focuses on the microbial ecology of extreme environments and the interaction of microorganisms with toxic metal(loid)s. She will be isolating and characterizing metal-reducing and exopolysaccharide-producing bacteria from the Nevada Test Site and using these organisms in sorption experiments with Pu.

James Begg—Postdoctoral fellow at LLNL. Dr Begg's expertise is in environmental radiochemistry and his research focuses on actinide sorption on inorganic phases, specifically Fe-oxides and clays.

4. Performance Milestones and Metrics

Table 4.1 shows the task plan schedule for five years for each of the five Program Elements. Each Program Elements is sub-divided into Tasks. However, all activities are closely integrated and as such, timing of specific experiments, especially as proposed in out years, may be modified. Blue demarcations show the original planned schedule and the green shows where we have deviated for the original plan. The accomplishments and metrics for each Program Element will be summarized below.

Table 4.1 Five year task plan subdivided into five Program Elements (A-E). The blue is the original plan, the green denotes where some projects were started earlier than originally planned, the lightest blue shows where projects have been delayed.



4.a Review of Scientific Progress

4.a.i Brief Review of Scientific Progress

Program Element A: Binary Sorption to High-Affinity Surface Sites

(M. Zavarin: lead; P. Zhao, S. Tumey, J. Begg)

The focus of Program Element A is the study of Pu sorption in simple binary systems at Pu concentrations ranging from those observed in the field (attomolar to picomolar) to those commonly used in the lab (nanomolar to micromolar). The hypothesis guiding the effort in Program A is the following:

Colloid-facilitated Pu transport is fundamentally controlled by binary surface-complexation phenomena occurring on sites that have a range of sorption affinities, site-specific sorption/desorption kinetics, and redox transformation rates.

Testing this hypothesis requires the collection of sorption data over a range of (1) solution conditions, (2) Pu concentrations, and (3) colloid minerals. The kinetics of sorption and desorption will be quantified and an understanding of the underlying mechanisms controlling sorption affinities and sorption/desorption kinetics identified. Based on the collected data, a surface complexation model that includes kinetics and hysteresis effects (if necessary) will be developed.

Task A1: Sorption Envelope and Isotherm Experiments

In FY10, Pu-sorption experiments were successfully performed with the environmentally common mineral goethite (FeOOH). These experiments were designed to not only quantify the sorption behavior of both Pu(IV) and Pu(V) over a ten order of magnitude concentration range but also to test the capabilities of the instruments at LLNL which are key to allowing us to probe Pu-mineral interactions at ultra-low concentrations. This comparison was completed in early FY11 (Fig. A1). We found that, below an equilibrium concentration of 10^{-9} mol/L, Pu sorption was linear and that Pu(IV) and Pu(V) reached equivalent sorption equilibria within 14 days. The linearity suggests that binary sorption to hypothetical high affinity sites at ultra-low Pu concentrations does not occur under these conditions (pH 8 NaCl/NaHCO₃ solutions). Whether this conclusion holds true over a wider range of solution conditions (e.g. ternary systems), reaction times, and mineral phases is the subject of ongoing research within this program.

At aqueous concentrations $>10^{-9}$ M, Pu(IV) “sorption” does not reach equilibrium within a 7-day experiment. The behavior can be attributed to a combination of surface-catalyzed reduction followed by surface precipitation and relatively slow homogeneous nucleation of Pu in solution. Homogeneous nucleation rates should increase with concentration due to an increasing thermodynamic driving force. On the other hand, surface catalyzed reduction and nucleation is limited by the access to surface sites at these concentrations. TEM characterization of these high concentration Pu sorption samples provide further insight into the surface precipitation of Pu on

goethite (Fig. A2). Importantly, epitaxial growth of Pu_4O_7 on goethite in Pu(IV) sorption experiments (Powell et al., 2011) was reproduced in these experiments. Furthermore, Pu(V) sorption experiments resulted in the same epitaxial growth of Pu_4O_7 . The relative abundance of Pu_4O_7 versus PuO_2 varied as a function of Pu concentration and initial oxidation state. Thus, the relative abundance of these two forms of Pu nano-colloids is controlled by the rates of homogeneous PuO_2 nucleation in solution, surface precipitation of Pu_4O_7 , and surface-catalyzed reduction of Pu(V) to Pu(IV).

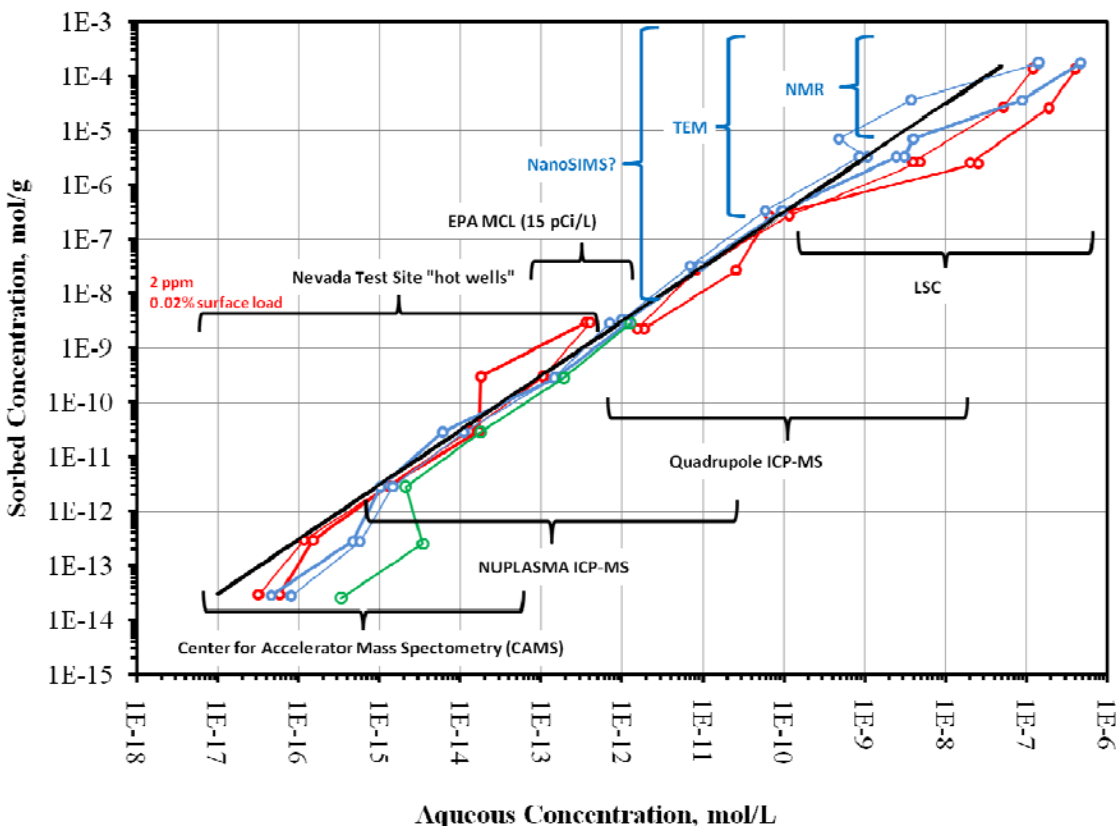


Figure A1. Pu(IV) (blue) and Pu(V) (red) sorption to goethite at 7 days (thick line) and 14 days (thin line). NuPlasma Pu(IV) data in green. All other low-level data collected by AMS.

With respect to comparing LLNL’s capabilities for ultra-low Pu measurement, we found that AMS detection limits were one to two orders of magnitude lower than the NuPlasma ICP-MS for an equivalent volume of sample. However, detectable Pu was measured by AMS in sample blanks, leading to large errors in the lowest concentration samples (Fig. A1). As a result, we are establishing access to low-level laboratories for all FY11 and future ultra-low Pu sorption experiments.

In FY11 the focus has been to replicate the goethite experiments using montmorillonite (a smectite clay) to determine whether observations made for the behavior of Pu in the presence of goethite hold true for other environmentally relevant mineral phases. These experiments consist of Pu(IV) and Pu(V) batch sorption isotherms with montmorillonite at initial Pu concentrations ranging from 10^{-7} to 10^{-17} M. This approach again makes use of the many Pu counting techniques available at LLNL, including accelerator mass spectrometry (AMS), NuPlasma HR IsoProbe mass spectrometry and quadrupole ICP-MS. Experiments are on-going and results are expected within the next three months.

Preliminary work from this task has examined Pu(V) removal from solution in systems containing 0.1 g/L and 1 g/L montmorillonite and initial Pu concentrations of 5×10^{-6} mol/L and 5×10^{-7} mol/L, which correspond to the highest adsorption isotherm concentrations. These experiments demonstrate that both the rate and extent of Pu(V) removal from solution was greater at 1 g/L solid compared to 0.1 g/L (Fig. A3). This is consistent with observations from FY10 goethite experiments where rate limited Pu(V) “sorption” at Pu concentrations above

10^{-9} M was attributed to a lack of available surface sites for surface catalyzed Pu(V) reduction. Interestingly, there is a difference in the percentage removal of Pu(V) from solution between the two starting concentrations. The system with an initial Pu(V) concentration of 5×10^{-6} mol/L showed a greater relative removal of Pu from solution after 30 days compared to the system with an initial Pu(V) concentration of 5×10^{-7} M. In previous experiments with goethite, it was suggested that at concentrations $>10^{-9}$ M, Pu removal from solution is driven by a combination of surface-catalyzed Pu(V) reduction and the homogeneous nucleation of Pu precipitates. As homogeneous nucleation rates are expected to increase with increasing Pu concentration due to an increasing thermodynamic driving force, the observed difference in Pu removal appears to highlight the importance of homogeneous nucleation in controlling Pu behavior in these systems.

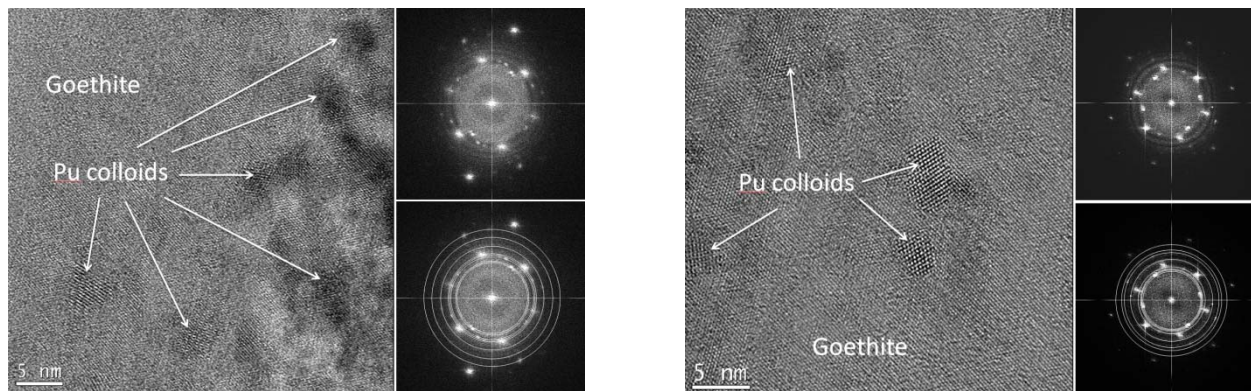


Figure. A2. Sorption of Pu(IV) (A) and Pu(V) (B) on goethite (7000 ppm) results in equivalent epitaxial surface precipitation of Pu_4O_7 .

A further outcome of this preliminary work was to help optimize the experimental parameters for the montmorillonite isotherm experiments, namely the solid:solution ratio to be used (1 g/L) and the equilibration time (30 days). Isotherm experiments are underway and will be completed in FY11. FY10 efforts identified high Pu backgrounds during sample preparation. As a result we are developing clean lab facilities to analyze samples at femtomolar concentrations using the CAMS facility.

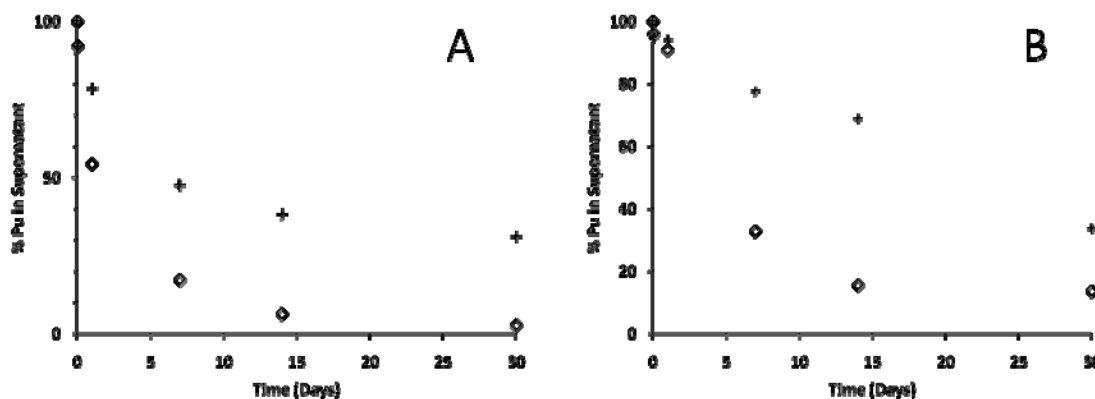


Figure A3. Pu(V) removal from solution in systems containing 0.7 mM NaHCO_3 /5 mM NaCl (pH \sim 8) and: 1 g/L montmorillonite (\diamond); 0.1 g/L montmorillonite (+). Experiments were spiked to initial Pu(V) concentrations of 5×10^{-6} M (A) and 5×10^{-7} M (B).

Continuing FY11/FY12 work will investigate the stability of surface-associated Pu through a series of flow-cell sorption/desorption experiments at femtomolar Pu concentrations. This work will complement the existing batch adsorption data as well as providing us with a unique opportunity to study the coupled adsorption-desorption processes impacting Pu behavior at environmentally relevant concentrations. These experiments will

also include a study of the stability of intrinsic Pu(IV) nano-colloids in the presence of montmorillonite to compare stabilities of adsorbed Pu, surface precipitated Pu, and intrinsic Pu nano-colloids.

Fundamental to our understanding of surface-catalyzed Pu(V) reduction and sorption to mineral surfaces in binary systems is the identity of the reductant (electron donor). Naturally occurring chemical species such as humic/fulvic acids have been shown to alter the oxidation state and mobility of Pu (Banik et al., 2007). However, the Pu(V) reductant in binary sorption experiments has not been identified even though its reduction has been quantified in the presence of a number of oxidizing and redox-neutral minerals (Powell et al., 2004; 2005; 2006; Zavarin et al., 2005; submitted). A candidate molecule that may affect Pu redox kinetics in “binary” systems is hydrogen peroxide. Hydrogen peroxide may be produced as a result of radiolysis (Morgenstern and Choppin, 1999) and is also present at trace levels in natural waters via photo-oxidation of organic matter, deposition from the atmosphere, or other processes (Zika et al., 1985; Cooper et al., 1988). Previous work has demonstrated the ability of peroxide to reduce Pu(V) in solution (Morgenstern and Choppin, 1999). However, the role of mineral surfaces in potentially catalyzing this process has not been studied. Experiments performed in FY11 with ultrapure corundum ($\alpha\text{Al}_2\text{O}_3$) with no known electron donor (pH 8) resulted in slow reduction of Pu(V) to Pu(IV). The addition of a large concentration of H_2O_2 enhanced the removal of Pu(V) from solution (Fig. A4). At high peroxide concentrations the presence of corundum does not increase reduction rates. However, factors such as H_2O_2 concentration, the solution pH, and the type of mineral surface may alter the effect of hydrogen peroxide. Previous studies examining arsenic behavior have found that the presence of H_2O_2 combined with Fe^{3+} can enhance the oxidation of As(III) (Voeglin and Hug, 2003; Pettine and Millero, 2000). The combination of H_2O_2 and Fe^{3+} may have a similar effect on Pu(IV). Indeed, preliminary experiments performed with goethite at pH 4 indicate that addition of hydrogen peroxide enhances desorption of Pu from the mineral surface, presumably by oxidizing surface associated Pu(IV) to Pu(V) (Fig. A5). Thus, it is clear that H_2O_2 may be considered an effective Pu(IV) oxidant or Pu(V) reductant depending on the specific aqueous and surface conditions present in a system.

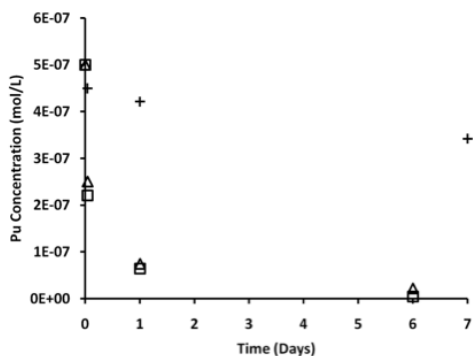


Figure A4. Pu(V) removal from solution in the presence of H_2O_2 and Al_2O_3 . Plot shows Pu(V) in solution (0.7 mM NaHCO_3 /5 mM NaCl at pH = 8) versus time.

(Δ) 1 g/L $\alpha\text{Al}_2\text{O}_3$; plus Pu(V)
 (\square) 1×10^{-3} M H_2O_2 ; plus Pu(V)
 (+) 1 g/L $\alpha\text{Al}_2\text{O}_3$ plus Pu(V).

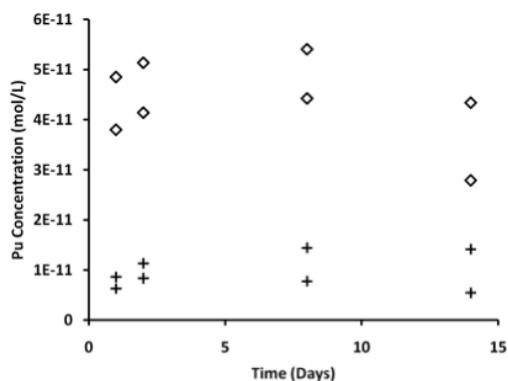


Figure A5. Desorption of Pu from goethite versus time. Initial sorption experiments contained 2 g/L goethite in 0.01 M NaCl at pH=4 and were spiked with 10^{-10} M Pu(IV). Solvent extraction on T = 14 d samples indicated that Pu was present in solution as Pu(V).

(+) 0.01 M NaCl at pH 4
 (\diamond) 0.01 M NaCl at pH 4 amended with 20 mM H_2O_2 .

Task A3: Ab-initio Modeling

At extremely low concentrations, there are no spectroscopic techniques that allow interrogation of the electronic structure of elements on mineral surfaces. Thus, we have embarked on a program of computational work employing a range of *ab initio* techniques including correlated wave function approaches (complete active space self-consistent field, CASSCF; multi-reference perturbation theory, MRPT) and density functional theory (DFT). We have also performed first-principles molecular dynamics within the DFT framework. Hardware resources available for this work include IBM BlueGene/L. Figure A6 is a schematic organization of various *ab initio* methodologies in terms of computational cost versus accuracy. Note that model force fields, commonly used, are not *ab initio*. *Ab initio* methodologies, although employ increasing cost (e.g. computational time), provide enhanced accuracy.

In general, the electronic structure of actinide (An) complexes poses numerous challenges for modeling. The high-Z elements exhibit large relativistic and spin-orbit coupling effects. The description of open-shell *f*-electrons is problematic due to strong correlation effects. Accurate treatment of actinide complexes often require sophisticated correlated wave function techniques whose cost grows rapidly with the number of electrons, and thus are only practical for the small systems. To date, most theoretical work has focused on the actinyl complexes AnO_2^+ and AnO_2^{2+} , for which detailed experiments in gas and aqueous phases are available for comparison and validation.

Methodologies with lower computational effort are possible (Fig. A6), but introduce uncontrolled approximations that require careful testing. The most common of these are based on DFT, which can potentially address larger and more complex systems. However, current approximations for exchange-correlation are not robust when applied to actinides. For example, DFT within the generalized gradient approximation (GGA) for solid PuO_2 oxide incorrectly yields a ground state that is metallic, when in fact it should be insulating. Hybrid functionals improve on this, giving the correct insulating ground state of solid PuO_2 . On the other hand, for the PuO_2^{2+} and PuN_2 molecules, DFT-GGA predicts ground state structures and vibrational frequencies that are in good agreement with multi-reference perturbation theory, while hybrid functionals exhibit *worse* agreement compared to DFT-GGA. Thus, before continuing on any extensive *ab initio* simulations, we first carried out benchmark studies.

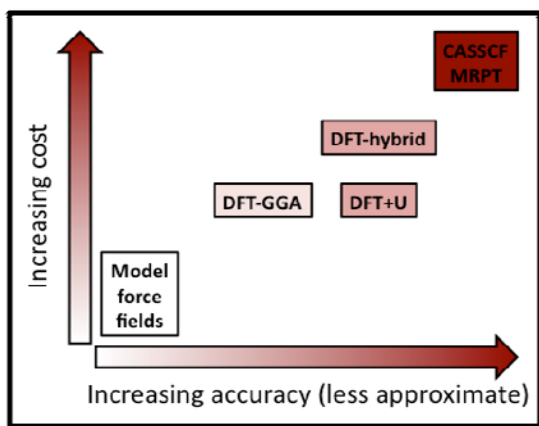


Figure A6: Schematic organization of various *ab initio* methodologies in terms of computational cost versus accuracy. Note that model force fields are not *ab initio*. Molecular dynamics with model force fields is commonly utilized for the simulation of aqueous geochemical systems; it is included here for comparison with the *ab initio* approaches that we employ in our work.

Our *ab initio* modeling efforts are currently focused on the atomic-scale behavior of monomeric $Pu(OH)_4$ in aqueous environments, which is expected to be the predominant species at $Pu(IV)$ concentrations of $< 10^{-10}$ M near neutral pH (Neck and Kim, 2001). Currently available spectroscopic techniques are not capable of detailed characterization at such low concentrations, and thus we turn to *ab initio* modeling to gain insights into the structure and chemical reactivity of monomeric $Pu(IV)$ at environmental conditions. However, the electronic structure of actinides poses numerous challenges for theory, and thus in FY10 we began with benchmark studies to evaluate the performance of various *ab initio* methodologies. We concluded that standard density functional

theory (DFT) within the generalized gradient approximation (GGA) provided a poor description of the electronic structure of $\text{Pu}(\text{OH})_4$. This is problematic, because *ab initio* simulations of condensed phases are most straightforwardly and efficiently carried out using the DFT-GGA.

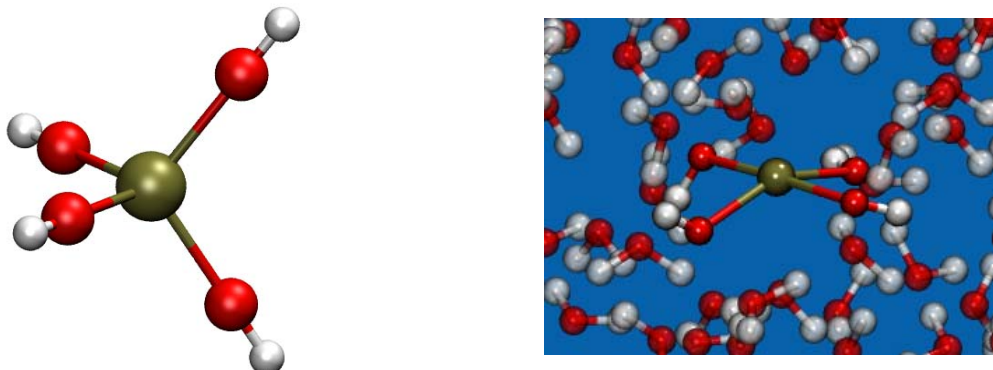


Figure A7, Left: Optimized $\text{Pu}(\text{OH})_4$ structure in the gas phase (i.e., no coordinated waters) is tetrahedral. The central gold atom indicates Pu, while red and white atoms denote O and H, respectively. Right: Snapshot from *ab initio* molecular dynamics simulation of $\text{Pu}(\text{OH})_4$ in a periodic simulation cell of 96 water molecules at ambient temperature and pressure. The presence of a bulk water environment stabilizes a distorted planar geometry for $\text{Pu}(\text{OH})_4$.

In FY11, we developed an approach for the *ab initio* simulation of $\text{Pu}(\text{OH})_4$ in aqueous environments based on DFT+U method. In short, this is an extension of standard DFT-GGA where an additional Hubbard-like term is included to describe the 5f electron correlations in Pu, while still retaining the computational efficiency of DFT-GGA. While the application of DFT+U to solid-state systems has a long history, here we propose to apply the DFT+U method to chemical problems in the liquid state. Our strategy follows from prior work on transition metal oxides (Mosey et al, 2008), where the parameters that enter into the DFT+U are calculated from first principles. A set of DFT+U parameters appropriate for aqueous $\text{Pu}(\text{OH})_4$ is determined by systematically evaluating a series of hydrated $\text{Pu}(\text{OH})_4(\text{H}_2\text{O})_n$ clusters of increasing size (up to $n=5$), which accounts for the dominant influence due to the first solvation shell of water.

We have successfully applied this DFT+U model to *ab initio* molecular dynamics (MD) simulations of $\text{Pu}(\text{OH})_4$ in a bulk water environment at ambient temperature (Huang et al, submitted 2011). In FY10, we found that the lowest energy structure for gas phase $\text{Pu}(\text{OH})_4$ is tetrahedral (Fig. A7, left), which is the geometry that minimizes the repulsion between the negatively charged OH^- ligands. On the other hand, our *ab initio* MD simulations for aqueous $\text{Pu}(\text{OH})_4$ indicate that the presence of a bulk liquid environment stabilizes a distorted planar structure (Fig. A7, right). This example illustrates the importance of explicitly including water in atomic-scale modeling of monomeric Pu(IV). Our current work now involves extending these simulations to examine the adsorption of monomeric Pu(IV) at a model mineral/water interface, starting with the diaspore/water interface as a structural analogue for the goethite/water interface.

Program Element B: Stabilization of Pu Surface Complexes on Mineral Colloids by Natural Organic Matter

(B. Powell: lead; R. Tinnacher, Students: L. Simpkins, J. Wong, T. Zimmerman)

The focus of Program Element B is to examine the influence of natural organic matter (NOM) on Pu sorption to pure mineral phases and sediments. The task is guided by the following hypothesis:

NOM can increase Pu mobility by 1) forming NOM coatings on colloids that stabilize Pu surface complexes and 2) formation of aqueous Pu-NOM complexes which decrease sorption of Pu and increase subsurface mobility.

The research plan consists of four tasks; the first two focus on equilibria of Pu-NOM (binary systems) and Pu-NOM-mineral (ternary systems) interactions. There is a strong coupling of these tasks with the binary (Pu-mineral) studies described in Program Element A.

Our FY11 milestone was to continue examination of the influence of NOM fractions on Pu sorption to pure mineral phases and to begin quantifying the data through aqueous and surface complexation modeling. We have met this milestone. Sorption experiments using gibbsite ($\alpha\text{-Al(OH)}_3$) and goethite ($\alpha\text{-FeOOH}$) have been performed using NOM surrogates such as Leonardite humic acid (HA), Suwannee River fulvic acid (FA), desferroxamine-B (DFOB), and citric acid (Task B1). We have begun interpreting the data in terms of an aqueous and surface complexation model. In FY11, we also determined stability constants for Pu-FA complexation (Task B2). The results from Task B1 have indicated that NOM can either enhance or decrease Pu sorption depending on specific NOM characteristics and chemical solution conditions, such as pH. To demonstrate the relevance of these effects on Pu subsurface mobility, we have begun some of the column experiments in Task B4. This is slightly ahead of schedule but deemed necessary to demonstrate the implications of some of the knowledge gained in Tasks B1 and B2.

Task B1: Screening for Enhanced Pu Mobilization by NOM

The objective of this task is to examine representative NOM surrogates (citric acid, desferroxamine-B, extracellular polymeric substances, FA, and HA) to determine their influence on Pu sorption to minerals and sediments. To date, our experiments have focused on Pu sorption to gibbsite ($\alpha\text{-Al(OH)}_3$) and goethite ($\alpha\text{-FeOOH}$). The overall observation is that NOM can cause either enhanced or reduced sorption to pure minerals depending on pH of the system, the character of the NOM, and the type of mineral involved. Particularly at low pH values, our data indicate that ternary surface complexes are forming and preliminary surface complexation constants have been determined. It also appears that smaller, more hydrophilic ligands such as citric acid and DFOB can stabilize aqueous Pu complexes more readily than larger ligands with both hydrophilic and hydrophobic components such as HA.

Influence of NOM on Pu sorption to gibbsite

The sorption of Pu to gibbsite in the presence of four types of NOM is shown in Figure B1. Previous experiments have shown nearly complete sorption of Pu(IV) to the mineral phase in ligand-free systems above pH 4 (Zimmerman, 2010; Powell et al., 2008). The data presented in Figure B1 shows that the presence of FA, DFOB, and citric acid causes an increase in aqueous Pu concentrations and a decrease in the Pu fraction sorbed relative to FA free systems. The most significant difference can be observed in the citric acid and DFOB systems. At low pH values, a slight increase in sorption relative to the ligand free system was seen in the presence of HA. This is consistent with the observations reported in the work done in FY10 (Zimmerman, 2010). Across the pH range 5-9, Pu sorption increases with increasing pH for systems containing FA, DFOB, and citric acid. In this region, the mineral surface charge transitions from a net positive to a net negative charge resulting in competition between the ligand and the surface for complexation/sorption of Pu(IV). Conversely, sorption of the ligand is expected to decrease with increasing pH (ligand-like sorption behavior). This was verified for FA (data not shown) and is consistent with anionic functional groups of FA interacting with positively charged gibbsite sites at low pH and being repelled by negatively charged sites at higher pH.

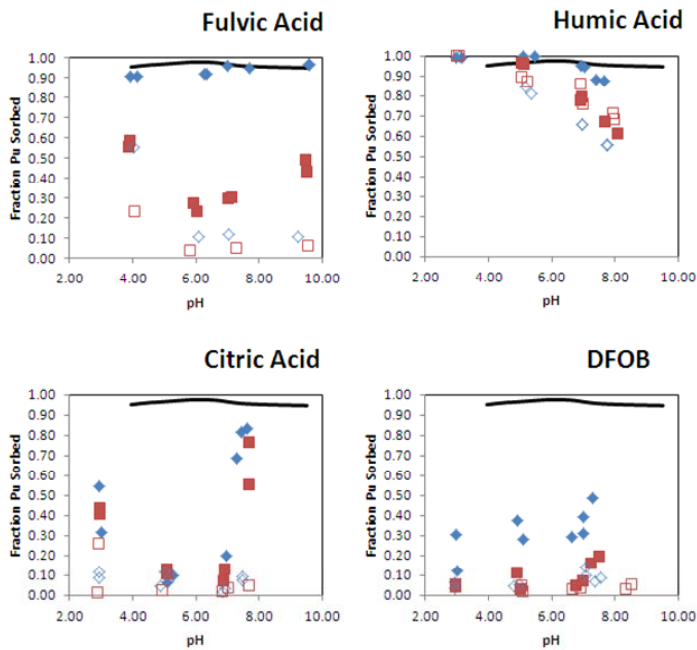


Figure B1: The effect of different ligands on the sorption of Pu(IV) to gibbsite. Data collected after a 7 day equilibration period. Solid phase separated from aqueous phase by 30k MWCO filtration. System parameters: Gibbsite concentration of 5 g/L; Pu-238 concentration of 10^{-10} M; 0.1 M NaCl background; 5mg_C/L (diamonds) and 50 mg_C/L (squares); closed symbols represent systems containing gibbsite and open symbols represent systems without gibbsite present. *Note: FA samples were prepared as mg FA/L. Therefore, the carbon concentrations are 2.62 mg_C/L and 26.22 mg_C/L. The solid line in each figure represents a surface complexation model for Pu-gibbsite developed from sorption data in the absence of NOM (Powell et al., 2008 and Zimmerman, 2010).

Influence of NOM on Pu sorption to goethite

In order to examine the influence of mineral characteristics on Pu sorption behavior, we also performed Pu sorption experiments to goethite. First experiments were set at pH 4 to evaluate the possibility of ternary surface complex formation, and to promote the potential formation of NOM coatings on the mineral surface. Enhanced sorption of Pu to goethite in the presence of FA was observed (Fig. B2), which is consistent with the formation of ternary surface complexes. The overall observation of ternary surface complex formation is consistent with Pu sorption behavior in gibbsite systems, as discussed above. However, the degree of enhanced Pu sorption at low pH is much greater, which reflects stronger binding of Pu-FA complexes to goethite than to gibbsite. This will be further examined in future years with hematite and corundum phases.

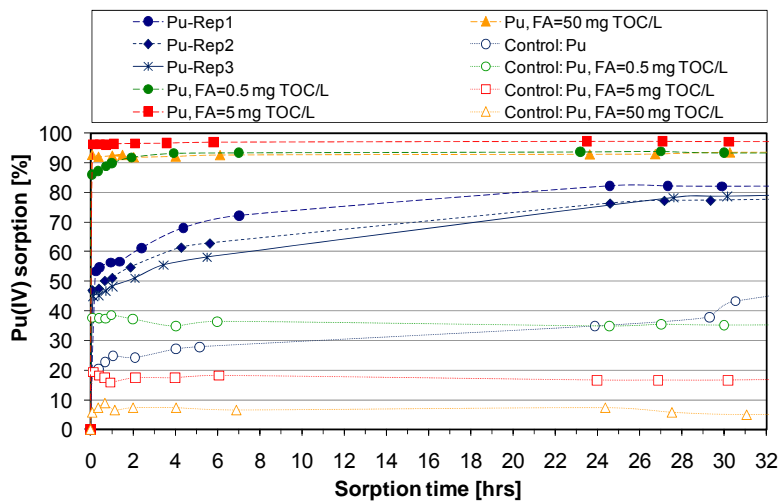


Figure B2: Sorption of 10^{-10} M Pu(IV) (initial oxidation state) to 2 g/L goethite in 0.01 M NaCl at pH=4 as a function of time and in the presence and absence of FA. Controls represent systems with the same chemical solution conditions but in the absence of goethite. The data indicate that both the rate and extent of Pu sorption are increased in the presence of FA.

Thermodynamic Modeling of Batch Sorption Systems

In order to examine the possible impact of ternary surface complexes and aqueous speciation, we developed thermodynamic models for the Pu-gibbsite systems discussed above. The first effort was to predict sorption of Pu(IV) in the presence of a ligand by assuming only the formation of Pu-AlOH surface complexes and Pu-ligand solution complexes. This modeling approach provided acceptable fits to the data at neutral and high pH values. This is expected based on the proposed sorption mechanisms occurring in each system. It is noteworthy

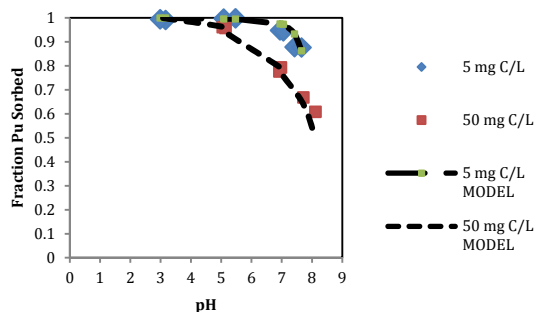
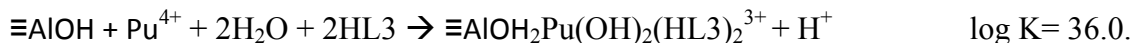


Figure B3: Data and model prediction of Pu sorption to gibbsite in the presence of HA. Data were modeled assuming the formation of ternary surface complexes.

that in most models, at high pH systems there is typically a point where Pu(IV) hydrolysis begins to occur, which outcompetes organic ligand complexation. This is manifested by increased sorption at high pH such as that observed in the Pu-gibbsite-citric acid system. The increase could also be due to formation of intrinsic PuO₂ colloids, although the systems are not necessarily saturated.

quantified in this task (Zimmerman, 2010). The final surface complexation constant and reaction are:



In all cases, a satisfactory fit to the low pH data was not achieved when using only binary surface reactions. Therefore, the data were remodeled and the formation of ternary surface complexes was included. An example of the model fits obtained is shown in Figure B3. This model is based on aqueous complexation by HA as previously

Task B2: Determination of Stability Constants for Relevant Pu-NOM Complex

Task B2 is focused on verifying and enhancing existing thermodynamic data for Pu-NOM complexation. Data for actinide binding to NOM are sparse. However, in order to quantify the fate and transport of Pu in subsurface environments, reliable aqueous complexation data are required. Similar to the Pu-HA constants determined in FY10 efforts (Zimmerman 2010), we determined Pu-FA stability constants using a discrete ligand binding approach. However, due to the overall low molecular weight distribution of FA as compared with HA, an ultrafiltration separation scheme was not possible; hence, a solubility-based approach was taken. Fulvic acid was added to saturated Pu(IV) systems in which PuO₂(s) was formed and the increase in aqueous Pu concentrations due to complexation with FA was monitored over time. To date, the samples have been equilibrating for 16 weeks, and as of 13 weeks, have not reached apparent equilibrium. The samples will continue to be monitored and after a steady state is reached, the stability constants will be determined. However, important kinetic dissolution data have been obtained from these experiments. The dissolution rate of PuO₂(s) in the presence of FA are shown in Figure B4. There is relatively little influence of pH within a range from pH 4 to 7.5 on the rate but the rate does increase with increasing FA concentration. This weak pH dependency is possibly explained by a relatively strong binding of Pu with FA across the entire pH region examined. This has also been observed for Pu-HA binding across the same pH range. The data show an initial rapid dissolution rate followed by a steady state dissolution rate of approximately 0.5 μg_{Pu}/L/day.

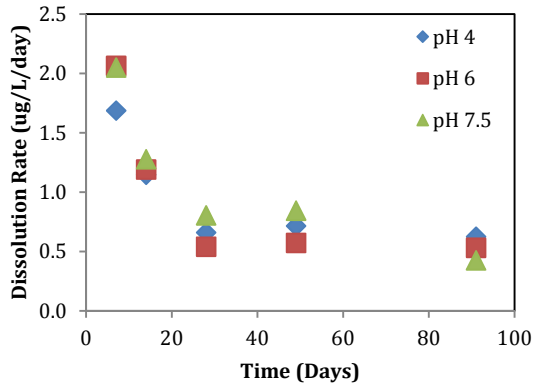
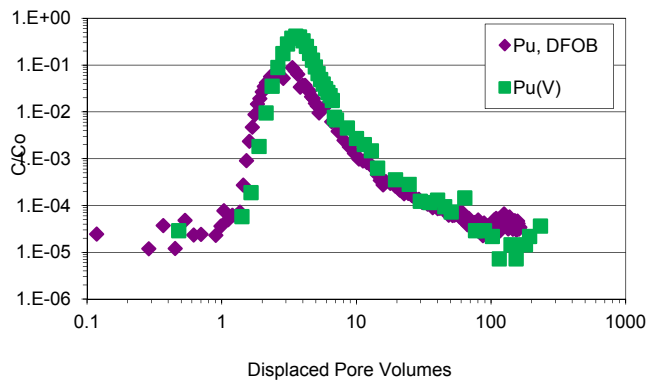


Figure B4: Dissolution rate of $\text{PuO}_2(\text{s})$ over time in 50 mg_C/L FA in a 0.1 M NaCl background. Solid phase separated from aqueous phase by 30k MWCO filtration. Dissolution rate was calculated by dividing the total Pu-242 concentration by the number of days of equilibration. A similar dataset with 5 mg_C/L FA is also available and shows a similar trend but a slightly slower rate indicating the influence of the FA concentration.

Task B4: Advective Transport of Pu in the Presence of Mineral Colloids and NOM

To demonstrate the potential for enhanced subsurface mobility due to the formation of soluble Pu-ligand complexes, a series of 1-D column experiments were performed. A subsurface sandy loam sediment from the Savannah River Site F-Area was packed into 8.3 cm x 1.5 cm columns and Pu-ligand complexes were injected as a one column volume finite step. Consistent with the enhanced sorption of Pu-ligand complexes at low pH values, the mobility of Pu in the presence of HA at pH 4 and FA at pH 5 was significantly decreased relative to a soluble Pu(V) system (data not shown). Data for Pu(V) were obtained from Powell et al., (2002). However, in a pH 7 system containing DFOB, Pu mobility was quite similar to that of soluble Pu(V) (Figure B5). Thus, consistent with batch sorption experiments, the mobility of Pu in the presence of NOM does appear to be profoundly influenced by the pH of the system. This is due to changes in Pu and NOM sorption affinities and in the relevance of Pu-NOM complexation reactions as a function of pH.



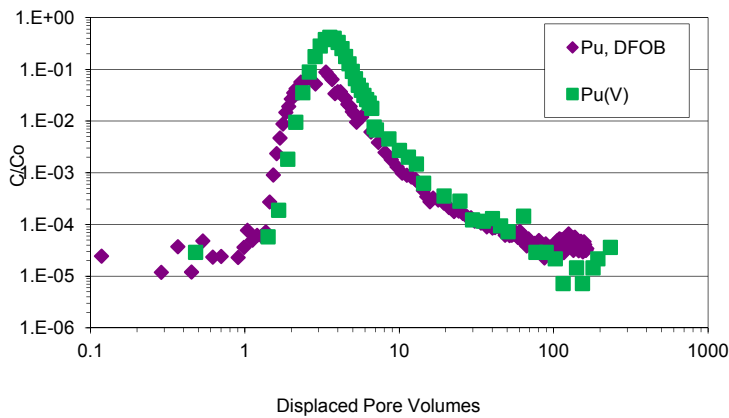


Figure B5: Normalized Pu concentration in column effluent indicating similar profiles of soluble Pu(V) and Pu(IV)-DFOB complexes. Note that in both cases Pu was added as a one column volume finite step. Pu(V) data from Powell et al., (2002).

Program Element C: Surface Precipitation of Pu Colloids: Experimental and Natural Nanocolloids

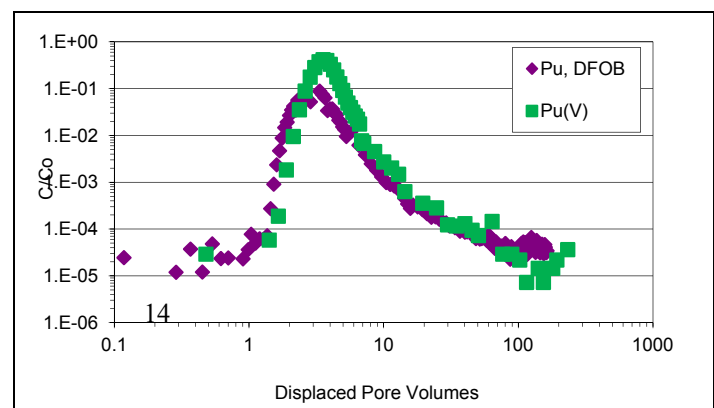
(A. Kersting: lead; B. Powell, Z. Dai, R. Kips, and P. Zhao)

The focus of Program Element C is to characterize the conditions under which Pu sorbs as a precipitate *versus* when it sorbs as monomeric surface complex. A second objective is to understand how our experimental findings compare with *natural* colloids contaminated with Pu at several field sites. This Program Element is strongly integrated with Program Elements A, B D and E. We are testing the following hypothesis:

The apparent sorption/desorption of Pu to mineral colloids is the result of surface precipitation of pure Pu nanopolymers. The stability/solubility of the Pu colloids will be affected by their depositional characteristics and interaction with the mineral surface.

The low solubility of Pu(IV) must be considered in any interpretation of laboratory sorption experiments conducted at relatively high concentrations ($>10^{-9}$ M) that could likely result in precipitation of PuO_2 polymer as a result of oversaturated solution conditions. Recent work by Neck *et al.* (2007) and Soderholm *et al.* (2008) sheds light on previously conflicting Pu(IV) solubility studies, suggesting that aqueous Pu(V) and 2- to 20-nm Pu colloids are expected to be present in solution. Thus, most laboratory Pu “sorption” experiments carried out at Pu concentrations greater than 10^{-9} M Pu(IV) should, in fact, be regarded as reflecting adsorption of Pu in multiple oxidation states and the interaction of colloidal Pu(IV) clusters with mineral surfaces.

In FY10 our experimental milestones were to finish our preliminary investigation of the structure of Pu(IV) colloids on goethite and silica and expand this effort to include Pu(V) (Task C1). Of particular interest is understanding what surface loading and aqueous concentrations results in incipient Pu polymerization at high Pu concentrations. An additional milestone was to initiate external collaborations to investigate natural colloids samples from a contaminated DOE site (Task C2). We completed all our milestones and started one additional collaboration involving examination of samples from Russia. The results of the first part of Task C1 were written up in manuscript form and recently published (Powell et al., 2011). For Task C2, samples from Hanford Reservation were analyzed by SEM and NanoSIMS as part of a new collaboration with Andy Felmy at (PNNL). In addition, aquifer solids from Tomsk, Russia, a radionuclide waste injection site, were analysed as a result of a new collaboration with Stepan Kalmykov at Moscow State University.

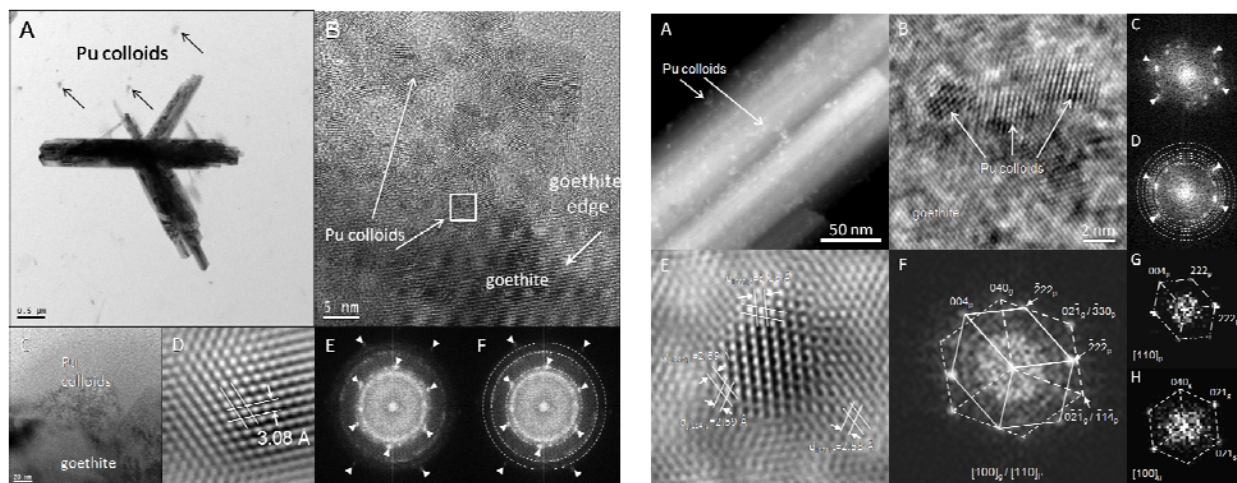


Task C1: Experimental Determination of Monomeric Versus Polymeric Pu Precipitation

In FY10 we completed a series of experiments focused on characterizing the chemical form of Pu on mineral surfaces. This work was submitted as a publication and published in FY11 (Powell et al., 2011). Particular emphasis was placed on identifying Pu concentrations and solution conditions that result in the formation of Pu colloids. In one study, the nanostructure of Pu colloids was investigated using high-resolution TEM for four different samples; 1) intrinsic Pu nano-colloids, 2) intrinsic Pu nano-colloids added to goethite colloids, 3) dissolved Pu(IV) added incrementally to goethite, and 4) dissolved Pu(IV) added incrementally to quartz.

Intrinsic Pu nano-colloids that were formed were 2-5 nm in diameter, and both electron diffraction analysis and HRTEM confirm the expected $Fm\bar{3}m$ space group with the fcc, PuO_2 structure. In the experiment in which intrinsic Pu nano-colloids were formed first and then mixed with goethite colloids, the majority of the Pu nano-colloids did not associate with goethite, but instead remained as colloid nanoclusters captured on the carbon film of the TEM grid. High-resolution TEM imaging (Fig. C1) and FFT analysis of the intrinsic Pu nano-colloids retained the same fcc PuO_2 structure as the original intrinsic Pu nano-colloids. In contrast, Pu nano-colloids formed by incrementally adding a dissolved Pu(IV) solution to a goethite suspension formed 2-5 nm nanoclusters on the mineral surface (Fig. C2). High-resolution imaging and electron diffraction analysis show that these nanoclusters do *not* have the expected $Fm\bar{3}m$ space group, but rather the $Ia\bar{3}$ space group, matching the bcc Pu_4O_7 structure.

The plutonium nano-colloids that formed on goethite have undergone a lattice distortion relative to the ideal fluorite-type structure, fcc, PuO_2 , resulting in the formation of a bcc, Pu_4O_7 structure. This structural distortion results from an epitaxial growth of the plutonium colloid on goethite, resulting in a stronger binding of plutonium to goethite compared with other minerals such as quartz for which this distortion was not observed. This finding provides new insight for understanding how molecular-scale behavior at the mineral-water interface may facilitate transport of plutonium at the field scale.



Figures C1 and C2. The composite figure, C1 (left) shows Pu colloids located off the goethite crystal with the expected the fcc, PuO_2 structure. C2 (right) shows Pu_4O_7 nano-colloids formed *in situ* on goethite.

The work continues in FY11. We are currently looking at Pu (IV) and Pu(V) colloids growing in the presence of Groutite (MnOOH) and Diaspore (AlOOH) in an effort to see if the structural distortion seen with the Pu oxide on goethite (FeOOH) exists with other minerals.

Task C2: Characterization of Pu on Natural Minerals Colloids

The objective of this task was to determine the form of the Pu found on environmental samples. In FY10 we initially demonstrated that we could use a combination of the SEM and NanoSIMS to image and detect low levels of Pu. We showed that we could detect Pu on goethite at 0.7 ppm. We also initiated a collaboration with Andy Felmy at PNNL, to characterize a series of highly contaminated soil samples collected beneath a Hanford

crib in an effort to determine how Pu is associated with the subsurface mineralogy. This project is quite challenging as concentrations are usually below detection limits, but the success will help to better understand how the Pu has been transported under a given set of geologic conditions.

Hanford Reservation, Washington State

We received samples from three different depths beneath a crib at the Hanford Reservation. These samples contained approximately 5 grams of sand/silt soils collected at depths 49 - 64 ft beneath the surface. An overview of the samples and their activity for ²⁴¹Pu, ²³⁹Pu and ²⁴¹Am, as measured by gamma spectroscopy, is given in Table C1.

Table C1. Hanford soil samples

Sample ID	depth	soil (g)	Am-241 (nCi)	Pu-241 (nCi)	Pu-239 (nCi)
B1HVC8	49-50'	5.96	152	below DL	45
B1HK15	63.5-64.5'	5.38	344	1516	382
B1HY61	> 65'	5.53	125	36	134

In FY10 several milligrams of contaminated soil were embedded in epoxy, polished, and analyzed by scanning electron microscopy (SEM) and NanoSIMS. Sample B1HK15 and B1HY61 had the highest activity according to gamma spectroscopy measurements (Table C1) and were therefore selected for initial analyses.

For the ion images from Hanford samples B1HK15 and B1HY61, the counts on *m/z* 239 were typically highest on the grain edges and were often, but not always, correlated with Fe (Fig. C5). The analyzed areas with 'hot spots' of *m/z* 239 were relocated on a secondary electron microscope for further investigation by energy-dispersive X-ray analysis (SEM-EDX). Identification of the mineral grains associated with the Pu is on-going. These efforts will help to correlate the counts at *m/z* 239 detected in the NanoSIMS with the different mineral phases.

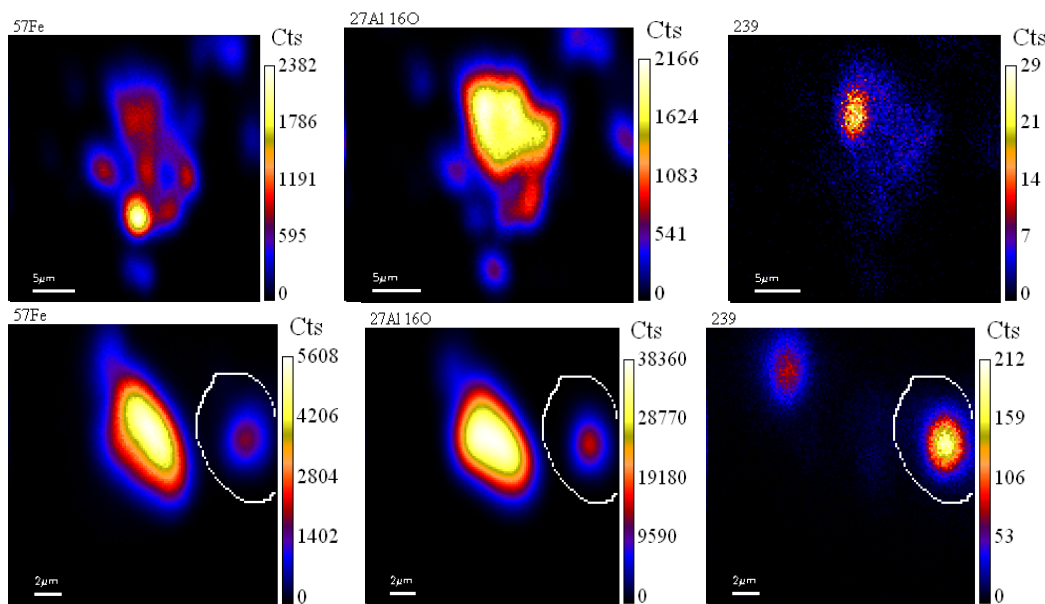


Fig. C5
Elemental maps
of 2 different
areas containing
Hanford soils. 20
x 20 um ion
images of ⁵⁷Fe,
²⁷Al, and ²³⁹Pu.

Although Pu-239 was detected on Hanford soil samples, the relative secondary ion intensities showed a different behavior than what was measured for the goethite+Pu standards described in our FY10 report. More specifically, the intensity of the $^{239}\text{Pu}^+$ ions was generally higher than the $^{239}\text{PuO}^+$ ions, which is unusual for sputtering with a primary oxygen beam. Given the very low count rate that was observed on m/z 255 relative to m/z 239, the possibility of unresolved mass interferences needs to be taken into account, especially for these mineral samples in which a wide range of elements is present. We are therefore exercising caution in the interpretation of these ion images, and in FY11 are developing and analyzing a new set of plutonium standards using different matrix materials (e.g., clays and quartz) that is more similar to the soil matrix.

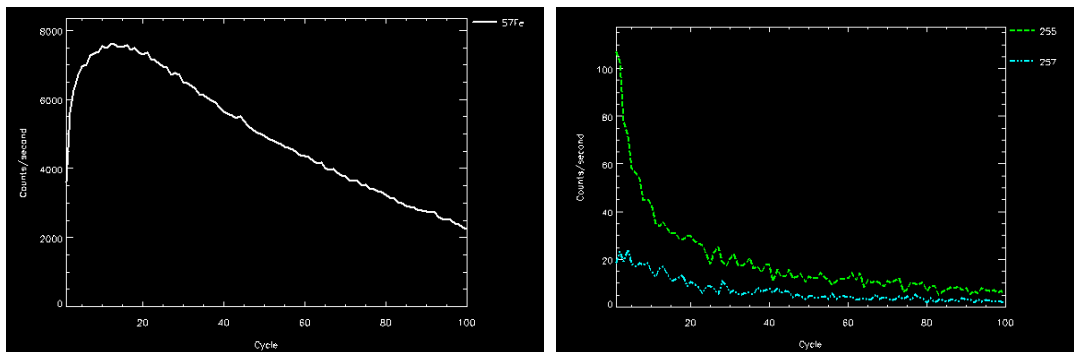


Figure C4. NanoSIMS depth profile of $^{57}\text{Fe}^+$ (left) and 255 ($^{239}\text{PuO}^+$) and 257 ($^{241}\text{AmO}^+$) obtained from sputtering a mixed Pu/Am goethite particle for several hours.

Program Element D: Co-precipitation with Altered Colloids

(S. Carroll: lead; H. Mason M., Zavarin and P. Zhao)

At the NTS, 98% of the Pu and other actinides deposited in the subsurface as a result of an underground nuclear test are thought to be sequestered by melt glass produced in the nuclear detonation. This Program Element is designed to investigate the Pu solubility and structure when the Pu is associated with colloidal silicates and nuclear melt glass from the NTS. Experiments conducted in this element will determine the conditions under which dissolved Pu concentrations are controlled by isomorphic substitution in secondary phases and those under which they are controlled by PuO_2 solubility (even at low concentrations). The hypothesis guiding the effort in Program D is the following:

Colloid formation during primary rock alteration and secondary mineral precipitation can structurally isolate Pu in colloids at environmental concentrations.

This Program Element consists of three tasks. Task D1 is designed to model the sorption of Pu at the silica/water interface at environmental concentrations. Given the difficulties in the experimental analysis of Pu sorption and co-precipitation at environmental concentrations, atomic-scale simulations are essential to clarify the nature of Pu aqueous speciation, sorption at mineral/water interfaces, and incorporation into the mineral framework. Task D2 involves using NMR and solution chemistry to probe the structural environment of Pu with inorganic, organic and microbial colloids. Task D3 is a series of experiments that alter and characterize nuclear melt glass from the NTS.

Task D1: Molecular Scale Simulations

For FY10 our milestone was to begin molecular-scale simulations taking advantage of advances in algorithms and computing hardware at LLNL that allow for the finite-temperature simulation of simple interfaces that explicitly include a liquid water layer. We have carried out first principles molecular dynamics simulations for the $\alpha\text{-Al}_2\text{O}_3(0001)$ /water interface, and our findings for the interfacial structure are consistent with synchrotron X-ray scattering experiments (Eng et al., 2000). This work has continued in FY11 and was presented above in Program Element A, Task A3: *Ab-initio* modeling.

Task D2: NMR and Solution Chemistry to probe Structural Environment of Pu

The NMR spectroscopic study of paramagnetic cation sorption as an analogue for Pu sorption

We have been developing NMR methods, which can be applied to the study of Pu interactions at the silica surface. A key challenge of using NMR spectroscopy to study the chemical structure of Pu at mineral surfaces is that Pu and its compounds exhibit paramagnetic electronic ordering which degrades the signal. However, comparing $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra of sorption samples to control samples synthesized in the absence of any paramagnetic cations should yield information about how the paramagnetic cations bind to the silica surface. We have investigated the sorption of the paramagnetic cations Co^{2+} , Cu^{2+} , and Ni^{2+} to the surface of amorphous silica using $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectroscopy. These systems have been chosen to serve as spectroscopic analogues of the Pu system. The $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS technique is surface selective since the protons exist only on the surface of the amorphous silica.

In FY11, individual spectra were collected for a control sample, and two Ni sorbed samples are presented in Figure D1. In these spectra we resolve three unique $^{29}\text{Si}/^1\text{H}$ environments, which we have labeled Q^2 , Q^3 , and Q^4 . Of these the Q^2 and Q^3 sites represent surface silanol sites where the paramagnetic cations can bind and the Q^4 site is an internal siloxane. We observe a significant reduction in the overall absolute intensity for all of the paramagnetic sorbed silica samples.

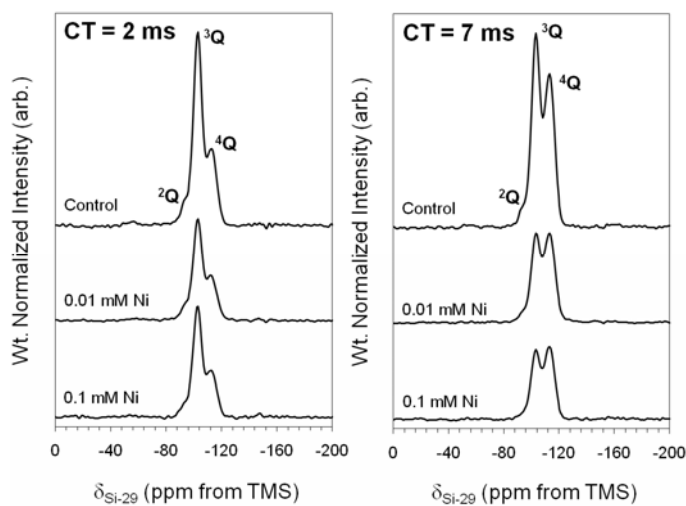


Figure D1. Stacked $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra collected at a CP contact time of 2 ms (left) and 7 ms (right) for (top to bottom) a control sample and two samples sorbed with different Ni concentrations. The spectra are all collected under identical acquisition conditions and are scaled to reflect their sample weight corrected absolute intensity.

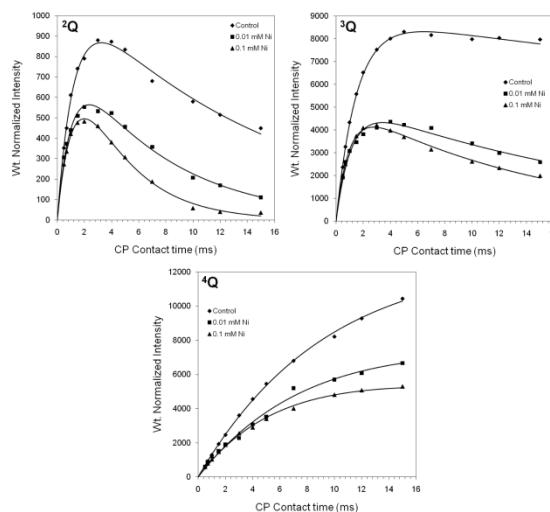


Figure D2. $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS kinetics curves produced for the Q^2 , Q^3 , and Q^4 silica sites for the control (\blacklozenge), 0.01 mM Ni (\bullet), and 0.1 mM Ni sample (\blacksquare). Solid lines represent least squares fit to a “classical” CP kinetics model. The data is scaled to reflect the sample weight corrected absolute intensities.

We also collected $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS spectra for all samples as a function of the CP contact time and the silica site specific CP kinetics data for each sorption sample (Fig. D2). In all cases, the curves collected for the paramagnet sorbed samples show significant deviation from those of the control samples. However, we note that the rates of the intensity increase for the Q^2 and Q^3 sites are invariant among the samples indicating that the sorption of the cations has little influence on average Si-OH bond lengths. The main differences apparent are the absolute magnitude of the intensity (I_0) and the decay constant ($T_{1\rho,\text{H}}$). A systematic decrease is observed in both the $T_{1\rho,\text{H}}$ and I_0 values with increasing paramagnetic cation concentration. These effects are largely due to the paramagnetic cations perturbing the ^1H spin population such that the intensity from the ^1H in closest association with the paramagnet species is lost resulting in a reduction of I_0 , but this paramagnet sufficiently alters the relaxation kinetics resulting in a reduction of $T_{1\rho,\text{H}}$. A sample where $\text{Ni}(\text{OH})_2$ colloids were physically mixed

with a control sample was also analyzed and the kinetic data is within experimental uncertainty from that of the pure control sample. These data indicate that the effects observed here must arise from the presence of direct bonds between the paramagnetic species and the silica surface, and not the presence of precipitates. Our results indicate that NMR spectroscopic methods can not only probe the interactions between paramagnetic ions and the amorphous silica surface at relatively low initial concentrations, but can also successfully differentiate between surface sorption and precipitation. In FY12 we will apply these same methods to investigate interactions between Pu and amorphous silica.

Task D3: Alteration of Pu-Containing Glass

Long-term alteration experiments of Pu-containing glasses (2 year experiments, with 6 month sampling) at 25 to 200C are underway using large volume (600 mL) in Titanium Parr bomb vessels. Gram quantities of Pu-containing glasses are being reacted to allow a thorough examination of secondary phases, characterization of Pu association, and follow-on Pu stability/desorption experiments. Characterization of Pu associated with secondary phases will be conducted by a combination of SEM, TEM, and NanoSIMS (e.g. Fig. D3).

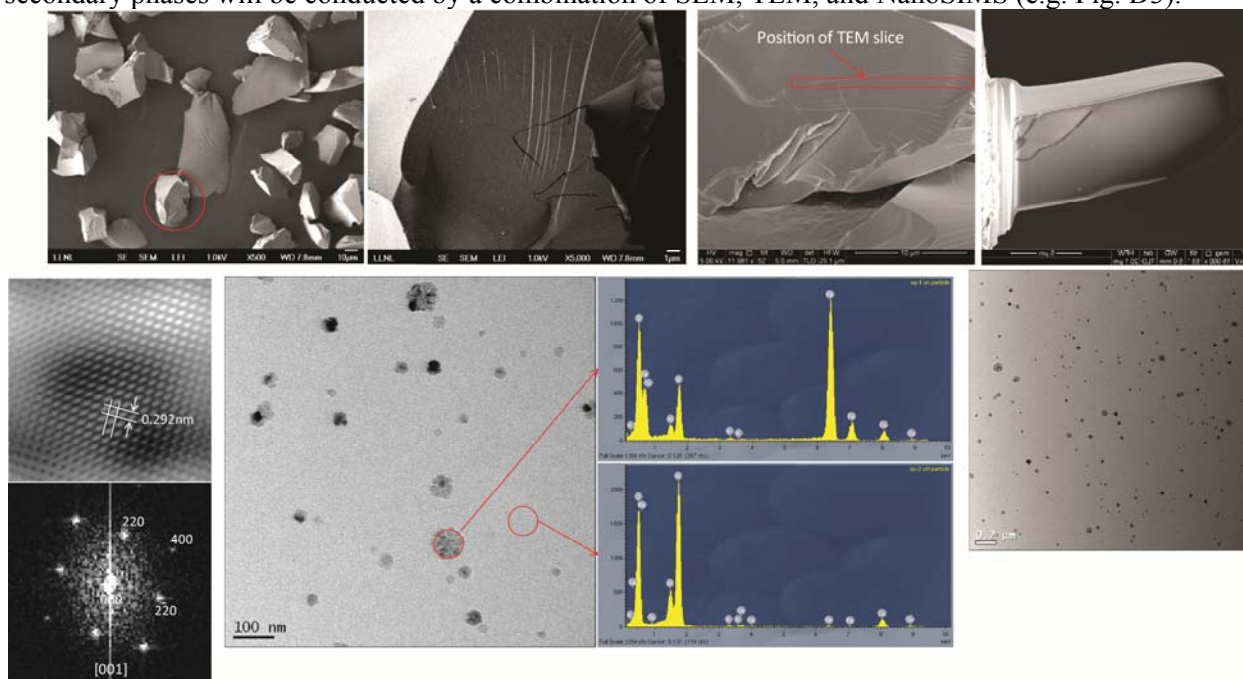


Figure D3. Initial characterization of Pu-containing glasses used in co-precipitation experiments. Unique combination of integrated SEM, FIB, and TEM capabilities used to identify magnetite nanoparticles in Pu-containing glass used in alteration experiments.

Program Element E: Direct and Indirect Microbial Interactions with Pu and Colloids (D. Moser, Lead; J. Fisher)

Microorganisms are associated with a variety of radioactive materials at DOE sites (Barnhardt et al., 1980; Francis et al., 1980; Fredrickson et al., 2004) and it is becoming well-known that Pu speciation and solubility are affected by microorganisms (Gillow et al., 2000; Neu et al., 2005; Panak and Nitsche, 2001). This Program Element tests the hypothesis that:

Environmental microorganisms can impact the mobility of Pu by direct and indirect mechanisms at environmentally relevant concentrations.

Most Pu microbiology to date has been performed on a handful of laboratory strains (Macaskie and Basnakova, 1998; John, 2001; Rusin et al., 1994; Francis, 2007; Panak and Nitsche, 2001) and at relatively high Pu concentrations (micromolar to millimolar). The general lack of knowledge concerning the

diversity, biodensity, exopolymer production potential, and direct Pu-reduction capacity of microorganisms at Pu-contaminated DOE sites is a knowledge gap that needs to be filled in order to assure that DOE's long-term stewardship goals are met.

In FY10 we met our milestones in Task E1 of screening a range of dominant microbial physiotypes from the Nevada National Security Site (NNSS, formerly the Nevada Test Site or NTS) despite limited hot well sampling opportunities. Three major objectives were to: identify the Pu-interactive microorganisms from the NNSS, determine if the isolated microorganisms can be grown in the lab, and produce and purify microbial organic matter (in this case extracellular polymeric substances, or EPS) to be used in the ternary sorption experiments with minerals, Pu, and NOM.

Task E1: Survey of Pu-Interactive Microorganisms

In addition to the direct effects of microorganisms, two indirect microbial processes (ligand production and mineral alteration) could influence Pu mobility at the NTS. It is well known that natural and artificial complexants impact the solubility of Pu (*e.g.*, Kersting et al., 1999). Microorganisms can produce a variety of such ligands (*e.g.*, siderophores (John, 2001) and extracellular polymeric substances (EPS) (Harper et al., 2008)) or may themselves be viewed as colloids because they fall within the appropriate size range (*e.g.*, 1 nm to 1 mm (Lawrence, 1996)). It is also well established that Pu interacts with mineral colloids (*e.g.*, clays, Fe-oxides) (Kesting et al., 1999, Novikov et al., 2006). Nevertheless, the question of how microbial weathering of these materials impacts actinide sorption remains unaddressed.

In FY10 we conducted both fieldwork and laboratory experiments that provided the starting material and baseline data for experiments conducted in FY11. UGTA field sampling (2 wells: ER-EC-11 (clean) and ER-20-7 (contaminated)) was limited to the last quarter of FY10. Additional wells: ER-20-8 and BILBY (clean), ER-20-5 #1 (high contamination), and ER-20-5 #3 (low contamination) were sampled in FY11 in conjunction with another DOE-funded project ((Moser PI, project ID, # 0016212). Laboratory experiments in FY2010 included enrichment for a variety of microbial physiotypes from NNSS and initial screening of NNSS organisms for Pu interaction. We also began the groundwork for examining the role of microbial organic matter that could promote or compete with Pu binding to natural surfaces. The inclusion of two "clean" wells in the FY11 sampling allowed us to estimate the number of subsurface microbes present at these sites by flow cytometry. Flow cytometry provides quantitative data on the number of cells present in a water sample, including the number of cells per milliliter and the fraction of those cells that are viable using two different cell staining methods. This method can only be used for non-radioactive samples, and was thus employed for enumerating cells from BILBY and ER-20-8. The density of cells from these sites was in the range of 10^4 cells mL⁻¹, with viable cells on the order of 10^3 mL⁻¹.

Archived fluids previously collected from the NTS (water from Tunnel U12N.10) were used to obtain microbial enrichments in FY10. Culturing, isolation, and characterization of bacteria from these samples and from fresh sample collections were performed during FY11. New microbial isolates were obtained from water collected from ER-20-7, and these and previously isolated organisms were identified by their 16S rRNA gene sequences (Fig. E1). The organism selected for production of natural organic matter (NOM) is a *Pseudomonas* sp. designated EPS1-W. *Pseudomonas* is a widely distributed genus common to soils and freshwater, and many relatives of our organism have been used previously for production of EPS. Many *Psuedomonas* spp. were also isolated from the NNSS (Rainier Mesa Tunnels) during previous microbial studies (Haldeman and Amy, 2003).

The major focus of our work in FY11 has been producing the EPS to be used in future experiments (Program Element B). Several methods for extracting and purifying EPS from a pure culture of *Pseudomonas* EPS1-W were tested and compared for 1) efficiency of EPS removal, 2) total EPS yield (based on TOC analysis), and 3) purity of EPS (*e.g.*, minimization of cell lysis). The final method selected was modified from a recently published method (Cao et al., 2011). Briefly, cells were grown as a biofilm on agar plates for 48 hours, washed from the plate with a saline buffer, and pelleted by centrifugation. Cell washing with both saline buffer and an EDTA-based buffer was employed to remove both loosely and tightly-bound EPS from the cells. EPS was filtered (0.22 μ m) to remove any cells, concentrated via 3 kD centrifugal filters, then precipitated with ethanol

overnight. Precipitated EPS was re-suspended with distilled de-ionized water, then dialyzed (2 kD) for 96 hours to remove any remaining salts and ethanol.

The quantity of EPS produced by each method was measured by TOC analysis conducted at LLNL. The quality of EPS was determined by the presence (or absence) of nucleic acids (an indicator of cell lysis). This analysis compares the spectrophotometric absorbance of EPS samples stained with 4',6-diamidino-2-phenylindole (DAPI), a fluorescent dye that binds to nucleic acids. Nucleic acid analysis was performed by LLNL and showed that the EPS samples contained little to no nucleic acid contamination (statistically the same as the negative control). Flow cytometry was also run on EPS-stripped cells to compare biomass (total numbers) to total viable cells (intact). These numbers were equivalent within the margin of error for replicates of each sample. Aliquots of these cells were plated on agar and grown overnight to confirm viability.

This method appears to yield both a high quantity and a high quality of EPS. Production and purification of EPS will continue, followed by a more complete chemical characterization to determine the structure of the EPS (molecular weight distribution, component sugars, associated proteins, etc.). A target of 1 g of (dry weight) EPS will be produced and archived for future experiments.

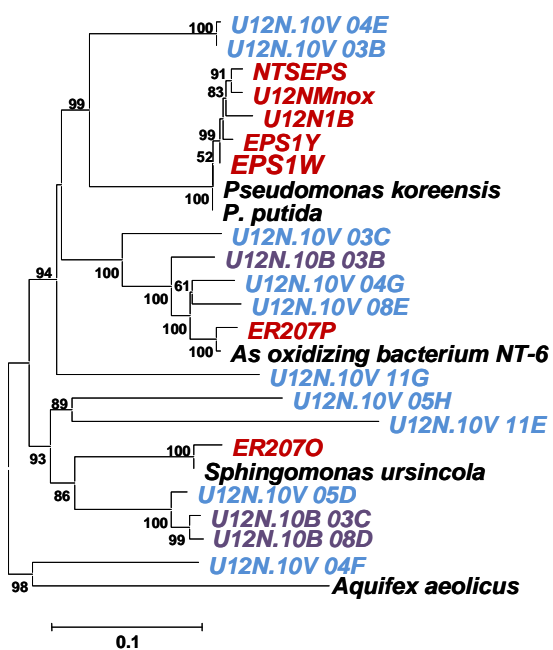


Figure E1. Phylogenetic tree of NNSS isolates from U12N.10 Tunnel and site ER-20-7 based on the 16S rRNA gene. Sequences in red are isolates; sequences in blue and purple are from environmental clone libraries, and sequences in black are characterized reference organisms.

EPS from one of the tested methods (lower yield) was used in a sorption experiment similar to those performed in FY10 with live, whole cells or lysed cells in solution with $\sim 10^{-9}$ M Pu. In the FY10 experiments, a high percentage (70-90%) of the Pu that was present sorbed to cells immediately (in 0.25 h) suggesting that biological material in the environment would also sorb Pu, even under transport conditions with low residence times/high flow rates. Pu remained sorbed after 24 hours. Lysed cells of *Shewanella* CN-32 had the highest K_d and sorbed the greatest percentage of Pu, possibly due to the increased surface area made available by compromised cell membranes. This observation is also important because it shows that cells do not need to take up Pu into the periplasm or cytoplasm to produce a biosorptive effect. Also notable were the higher K_d values for treatments with higher EPS contents, suggesting that Pu may sorb primarily to EPS as has been shown for other actinides.

In the FY11 experiment, ~ 0.01 mg of EPS was mixed with Pu in a low pH (< 5) solution and placed in Slide-a-lyzers (self-contained dialysis units), then dialyzed over the course of 48 hours. Over 85% of Pu was retained

inside the membrane with the EPS. These experiments will be repeated at more environmentally relevant pH (7.5-8) at the end of FY11 following production and characterization of EPS.

4.a.ii Scientific Highlights

Successful measurement of Pu at ultra-trace levels using CAMS. Plutonium-goethite sorption experiments were performed to aqueous concentrations below 5×10^{-17} M, equivalent to the detection of 3×10^6 atoms in a 100 mL sample. This CAMS capability will allow us to readily perform laboratory experiments that cover the range of environmental Pu concentrations of interest.

Ternary Pu-NOM-gibbsite (AlOH₃) sorption experiments demonstrated the mobilization of Pu as a result of aqueous complexation over a pH range of 5-9. The degree of Pu mobilization by NOM (DFOB > crtric acid \approx fulvic acid > humic acid) reflects the stability of the binary aqueous complexes.

Demonstrated Pu detection using NanoSIMS at concentrations as low as 0.7 ppm Pu on goethite. This is well below the concentrations at which Pu nano-colloids were observed by TEM and surpassed expectations outline in the SFA proposal. As a continuation of this work, in FY11 we successfully imaged nanometer-scale Pu distribution on Hanford sediments located 60 feet beneath a disposal crib using the NanoSIMS. Additional work to identify the mineral association of Pu will greatly help us understand how Pu moves in the subsurface.

Identified Pu nano-colloids lattice distortion when sorbed to goethite resulting in the formation of a bcc, Pu₄O₇ structure. This distortion results from an epitaxial growth of colloidal plutonium on goethite and provides new insight into the molecular scale behavior of Pu and how that may facilitate its transport in the subsurface. Powell et al., 2011 *EST*45(7) pp 2698-2703. As a continuation of this work, in FY11 we demonstrated that a similar distortion occurs with Pu(V) surface reduction to Pu(IV) on goethite.

Applied first-principles, Ab initio, modeling. Showed that in an aqueous environment the planar form of Pu(OH)₄ isomer can potentially be stabilized over the tetrahedral form (paper submitted).

4.a.iii Summary of Publications

Publications were highlighted in each Program Element where appropriate. To summarize, we published 2 papers, 2 have been accepted and 1 is in press. We presented 11 presentations at national meetings (1 invited).

Powell, B.A., Zurong Dai, Mavrik Zavarin, Pihong Zhao, Annie B. Kersting. (2011) Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces, *ES&T* 45 (7), pp 2698–2703

Zhao P., Zavarin M., Leif R., Powell B., Singleton M., Lindvall R., and Kersting, AB. (2011). Mobilization of actinides by dissolved organic compounds at the Nevada Test Site *Applied Geochemistry*. 26:3 308-318

Tinnacher, R. M.; Zavarin, M.; Powell, B. A.; Kersting, A. B. (2011) Kinetics of Neptunium(V) Sorption and Desorption on Goethite: An Experimental and Modeling Study, Accepted *Geochimica et Cosmochimica Acta*, .

Kersting, A.B. and Zavarin, M. (2011) Chapter: Colloid Facilitated Transport of Plutonium at the Nevada Test Site, NV, USA. In: Actinide Nanoparticles Research. Ed. Kalmykov, S. and Denecke, M. In press. *Springer*.

Huang, P., Zavarin, M., and Kersting, A.B. *Ab initio* electronic structure of Pu(OH)₄: Comparison between density functional and multi-reference theories. *Submitted*, 2011.

Snow, M. et al. *Neptunium Sorption to Goethite*. LLNL summer student poster session, Aug. 8, 2010 LLNL-POST-448451.

Zhao, P. et al. *Pu Sorption to Goethite at Micromolar to Attomolar Concentrations*. Poster Pu Futures-The Science, Sept 19-23, 2010, Keystone CO

Tinnacher, R. M.; Zhao, P.; Williams, R. W.; Zavarin, M., Kersting, A. B. Neptunium-237 Concentrations in Groundwater from Nevada Test Site Wells. Poster Pu Futures: The Science 2010, Keystone, CO, 19-23 Sept. 2010.

Tinnacher, R. M.; Powell, B. A.; Kersting, A. B.; Zavarin, M. A New Approach to Simulate the Kinetics of Metal Desorption from Mineral Surfaces. Talk AGU Fall Meeting, San Francisco, CA, 13-17 Dec. 2010.

Honeyman, B. D.; Tinnacher, R. M. Changes in the Kinetics of Uranium(VI) Sorption Reactions to Mineral Surfaces in the Presence of Fulvic Acid. Poster AGU Fall Meeting, San Francisco, CA, 13-17 Dec. 2010.

Zhao, P. et al. *Isotherm of Pu/Goethite System: Linearity and Sorbent Surface Characterization*. Poster AGU, San Francisco, Dec. 15-19, 2010

Fisher, J. et al. *Microbially Produced Organic Matter and Its Role in Facilitating Pu Transport in the Deep Vadose Zone*. Talk AGU, San Francisco, Dec. 15-19, 2010

Kersting, A.B.; Powell, B.A.; Zavarin, M.; Zhao, P.; Dai, Z. *Structure of plutonium oxide on mineral surfaces*. Invited talk. Pacificchem, Dec. 11-17, 2010.

Simpkins, L.; Powell, B. A. *Effect of fulvic acid on the sorption of plutonium to minerals*, Pacificchem, Dec. 11-17, 2010

Powell, B.A.; Zimmerman, T. N.; Simpkins, L. A.. *Modeling plutonium interactions with complex molecules and interfaces*. Pacificchem, Dec. 11-17, 2010

Mason, H. E., Maxwell, R. S., and Carroll, S. A. *Development of a $^{29}\text{Si}\{1\text{H}\}$ CP based surface specific technique for actinide sorption studies*. American Chemical Society Fall Meeting, August 28 – September 1st, Denver, CO, 2011.

4.b Future Scientific Goals

Program Element A: We will complete the Pu sorption experiments on montmorillonite clay that parallel the experiments with goethite and build upon earlier high concentration studies. In FY12 we will begin quantifying desorption rates using goethite and/or montmorillonite in a flow-cell apparatus. *Ab initio* modeling effort will continue to focus on simulation of monomeric Pu on simple mineral surfaces and in the presence of water.

Program Element B: We will study Pu-EPS and continue to study Pu-fulvic acid aqueous complexation and quantify complexation constants. We will examine the effect of ternary systems on sorption/desorption kinetics with different NOM and Pu.

Program Element C: We continue our investigation of Pu epitaxial growth on different mineral surfaces with aluminum analog of goethite (diaspore, $\alpha\text{-AlOOH}$) and groutite (MnOOH). We will continue to evaluate Hanford sediments using NanoSIMS.

Program Element D: Sampling and characterization of secondary minerals produced during long-term melt-glass alteration experiments will be conducted. TEM will be employed to identify the location of the Pu on the secondary minerals. Secondary minerals will be isolated and used in flow-cell experiments to characterize desorption behavior. NMR studies will examine Pu interactions with amorphous silica.

Program Element E: Ternary sorption experiments using microbial exudates isolated from the Nevada Test Site contaminated wells will be used in sorption/desorption experiments with Pu at LLNL. We are moving our experimental program to LLNL because DRI is not able to work with radioactive samples and that is required for the next stage of work. See 4.d for more details. We will compare these next experiments with experiments in Program Element B.

4.c New Scientific Results See section 4.a.ii

4.d. Collaborative Research Activities

We have two sub-contracts to collaborate with two external research groups. The first is with Brian Powell at Clemson University, SC to work on Program Element B. Details of the work are discussed in section 4.a.i, Program Element B. The second sub-contract is with Duane Moser from the Desert Research Institute, NV to work on Program Element E. Details of the work are discussed in section 4.a.i Program Element E.

Going forward in FY12, we will be conducting the microbial work at LLNL. We will close out the sub-contract with DRI but will continue to provide access to the NTS for D. Moser through LLNL's work authorization packages and safety protocols. We have hired a postdoc who is a microbiologist and will be supervised by Dr. Yongqin Jiao, who joined our program last year. He will start in January, 2012 and will be working ½ time on our program and ½ time on Dr. Jiao's program. We believe this change retains the same level of expertise in microbial systems while allowing us to proceed doing experiments with low doses of radioactivity.

We initiated two unfunded research collaborations to investigate contaminated samples from Hanford with Andy Felmy (PNNL) and Tomsk, Russia with Stepan Kalmykov (Moscow State University. Details and results from these collaborations can be found in Section 4.a.i, Program Element C, Task C2.

We had 2 summer students in FY10. Mathew Snow, who subsequently was awarded a Nuclear Forensics Graduate Fellowship to work with Sue Clark at Washington State. He returned in the summer of FY11 to write up his research results for publication. We have 2 new summer students in FY11. They will both be completing an experimental project on actinide environmental radiochemistry.

5. Staffing and Budget Summary

5.a Funding Allocation by Program Element

5.a.i Present Funding

Our SFA is currently funded at 1.2M/yr for 5 years beginning Oct. 2009. We had approximately 200K carry-over in FY11. The amount spent in FY11 is projected to be:

<u>Program Element</u>	<u>Costs (K)</u>	<u>LLNL Researcher</u>	<u>Effort</u>	<u>Cost (K)*</u>
Program Element A	400	Annie Kersting	15%	100
Program Element B (Subcontract Clemson Univ.)	150 120	Mavrik Zavarin	60%	240
Program Element C	180	Pihong Zhao	60%	195
Program Element D	215	Patrick Huang	50%	160
Program Element E (Subcontract DRI)	160	Zurong Dai	20%	100
		Scott Tumey	10%	20
		Ruth Kips	50%	80
		Ruth Tinnacher	75%	150
		James Begg	75%	150
		Harris Mason	30%	60
Total	1.2K	LLNL effort		1.25K*

*Effort costs for LLNL staff do not include supplies, analytical costs or travel. We expect to have approximately 100K carry-over for FY12 Oct start.

5.b Funding for External Collaborators

External collaborators are: Brian Powell at Clemson University, SC. He is funded by a sub-contract for \$120K/year for work in Program Element B. He completed his milestones. Our second collaborator is Duane Moser from Desert Research Institute, NV. He is funded at \$160K/yr for work in Program Element E. He completed his milestones. The effort with U. Clemson will continue at approximately the same level of funding. The funding with Desert Research Institute will end and experiments using Pu in Program Element E will continue at LLNL in FY12.

5.c Personnel Actions

Most of our staff continued on in FY11 from FY10 efforts. This includes 8 staff scientists, 4 postdocs and 1 student at LLNL. Collaborations from 2 other institutions were also initiated that include 2 lead scientists, 1 postdoc and 3 graduate students. As part of our efforts to encourage young investigators and hire new staff, we converted one LLNL postdoc to a flex-term staff scientist in April, 2011. We hired one new postdoc in August, 2010. We currently have an opening for one additional postdoc.

5.d National Laboratory Investments

The Seaborg Institute covers all of the administrative costs to execute this program, and approximately 10% of an Administrator's time. In addition, the SEM operational cost is also covered under the Institute's operating budget. Annie Kersting, Director of the Seaborg Institute oversees a summer student program that paid for the cost of one summer student working on this program in FY10.

As an institution, LLNL subsidizes the cost of all postdoc by 25%.

Several pieces of equipment were purchased in FY10 and FY11 by other programs that will directly benefit BER. They are: low energy gamma counter (Canberra), BET (Quantachrome Quadrasorb with low surface area Kr option), XRD and Deltech furnace (glass synthesis applications). All equipment is available for this program. LLNL has committed to refurbishment of Building 151 (the primary location of SFA facilities).

This will involve laboratory refurbishment and modernization, as well as the purchase of new analytical instruments. As part of this renovation, a new low-level lab will be constructed for use by this SFA.

5.e Capital Equipment

Capital equipment purchases were not made in FY11.

6. References

- Banik, N. L., R. A. Buda, S. Burger, J. V. Kratz, and N. Trautmann (2007), Sorption of tetravalent plutonium and humic substances onto kaolinite, *Radiochimica Acta*, 95(10), 569-575.
- Barnhart B.J., Campbell E.W., Martinez E., Caldwell, and Hallet. (1980) Potential microbial impact on transuranic wastes under conditions expected in the Waste Isolation Pilot Plant (WIPP). In Annual Report. Los Alamos National Laboratory.
- Cao, B., Shi, L., Brown, R.N., Xiong, Y., Fredrickson, J.K., Romine, M.F., Marshall, M.J., Lipton, M.S., Beyenal, H. (2011) Extracellular polymeric substances from *Shewanella* sp. HRCR-1 biofilms: characterization by infrared spectroscopy and proteomics. *Environmental Microbiology* 13(4): 1018-1031.
- Cooper, W. J., R. G. Zika, R. G. Petasne, and J. M. C. Plane (1988), Photochemical formation of H₂O₂ in natural waters exposed to sunlight, *Environ. Sci. Tech.*, 22, 1156-1160.
- Demirkanli D.I, Molz F.J., Kaplan D.I., and Fjeld R.A. (2008) A fully transient model for long-term plutonium transport in the Savannah River Site vadose zone: Root water uptake. *Vadose Zone Journal* 7(3), 1099-1109.
- Eng P.J. et al., (2000) *Science* 288, 1029
- Francis A. J., Dobbs S., and Nine B. J. (1980) Microbial Activity of Trench Leachates from Shallow- Land, Low-Level Radioactive-Waste Disposal Sites. *Applied and Environmental Microbiology* 40(1), 108-113.
- Francis A. J. (2007) Microbial mobilization and immobilization of plutonium. *Journal of Alloys and Compounds* 444, 500-505.
- Fredrickson J. K., Zachara J. M., Balkwill D. L., Kennedy D., Li S. M. W., Kostandarithes H. M., Daly M. J., Romine M. F., and Brockman F. J. (2004) Geomicrobiology of high-level nuclear waste contaminated vadose sediments at the Hanford Site, Washington State. *Applied and Environmental Microbiology* 70(7), 4230-4241.
- Gillow J. B., Dunn M., Francis A. J., Lucero D. A., and Papenguth H. W. (2000) The potential of subterranean microbes in facilitating actinide migration at the Grimsel Test Site and Waste Isolation Pilot Plant. *Radiochimica Acta* 88(9-11), 769-774.
- Glynn P. D. (2003) Modeling Np and Pu transport with a surface complexation model and spatially variant sorption capacities: Implications for reactive transport modeling and performance assessments of nuclear waste disposal sites. *Computers & Geosciences* 29(3), 331-349.
- Haldeman, D.L., and P.S. Amy. (1993) Bacterial heterogeneity in deep subsurface tunnels at Rainier Mesa, Nevada Test Site. *Microbial Ecology* 25:183-194.
- Harper R. M., Kantar C., and Honeyman B. D. (2008) Binding of Pu(IV) to galacturonic acid and extracellular polymeric substances (EPS) from *Shewanella Putrefaciens*, *Chlostridium* sp. and *Pseudomonas fluorescens*. *Radiochimica Acta* 96, 753-762.
- John S. G., Christy E. Ruggiero, Larry E. Hersman, Chang-Shung Tung, and Mary P. Neu. (2001) Siderophore mediated plutonium accumulation by *Microbacterium flavescens* (JG-9). *Environmental Science & Technology* 35, 2942-2948.
- Kaplan, D.I., Powell B.A., Demirkanli D.I., Fjeld R.A., Molz F.J., Serkiz S.M., and Coates J.T. (2004) Influence of oxidation states on plutonium mobility during long-term transport through an unsaturated subsurface environment. *Environmental Science & Technology*. 38(19), 5053-5058.
- Kaplan, D.I., Powell B.A., Gumapas L., Coates J.T., Fjeld R. A., and Diprete D.PI (2006) Influence of pH on plutonium desorption/solubilization from sediment. *Environmental Science & Technology* 40(19), 5937-5942.
- Kersting A. B., Efurud D. W., Finnegan D. L., Rokop D. J., Smith D. K., and Thompson J. L. (1999) Migration of plutonium in ground water at the Nevada Test Site. *Nature* 397(6714), 56-59.
- Lawrence J. R. H. M. J. (1996) Transport of bacteria through geologic media (review). *Can. J. Microbiol.* 42, 410 - 422.
- Macaskie L. E. and Basnakova G. (1998) Microbially enhanced chemisorption of heavy metals: A method for the bioremediation of solutions containing long lived isotopes of neptunium and plutonium. *Environmental Science & Technology* 32(1), 184-187.
- Morgenstern, A. and Choppin, G.R., 1999. Kinetics of the reduction of Pu(V)O₂⁺ by hydrogen peroxide. *Radiochimica Acta* 86, 109-113.
- Mosey, N.J.; Liao, P., and Carter, E.A. (2008). Rotationally invariant ab initio evaluation of Coulomb and exchange parameters for DFT+U calculation. *J. Chem. Phys.* 129, 01410
- Neck V. and Kim, JL (2001). Solubility and hydrolysis of tetravalent actinides. *Radiochim Acta*. 89: 1-16.

- Neck V., Altmajer M., Seibert A., Yun J.I., arquardt C.M., and Fanghanel T. (2007) Solubility and redox reactions of Pu(IV) hydrous oxide: Evidence for the formation of PuO₂+X (s, hyd.) *Radiochimica Acta* 95(4), 193-207.
- Neu M. P., Icopini G. A., and Boukhalfa H. (2005) Plutonium speciation affected by environmental bacteria. *Radiochimica Acta* 93(11), 705-714.
- Novikov, A.P., Kalmykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V., Myasoedov, B. F. Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia, *Science* 314, 638 (2006).
- Panak P. J. and Nitsche H. (2001) Interaction of aerobic soil bacteria with plutonium(VI). *Radiochimica Acta* 89(8), 499-504.
- Pettine, M. and Millero, F.J., 2000. Effect of metals on the oxidation of As(III) with H₂O₂. *Marine Chemistry* 70, 223-234
- Pickett D.A. (2005) Approach to assessing the potential effects of colloidal radionuclide transport on nuclear waste repository performance. *Nuclear Science and Engineering* 151(1), 114-120.
- Powell, B. A., R. A. Fjeld, D. I. Kaplan, J. T. Coates, and S. M. Serkiz (2005), Pu(V)O₂⁺ adsorption and reduction by synthetic hematite and goethite, *Environmental Science & Technology*, 39(7), 2107-2114.
- Powell, B. A., R. A. Fjeld, D. I. Kaplan, J. T. Coates, and S. M. Serkiz (2004), Pu(V)O₂⁺ adsorption and reduction by synthetic magnetite (Fe₃O₄), *Environmental Science & Technology*, 38(22), 6016-6024.
- Powell, B. A., et al. (2006), Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain tuff, *Environmental Science & Technology*, 40(11), 3508-3514.
- Powell, B. A., Fjeld, R. A., Coates, J. T., Kaplan, D. I., Serkiz, S. M. "Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment (U)," WSRC-TR-2003-00035, Westinghouse Savannah River Company, U.S. D.O.E. Savannah River Site, December 2002.
- Powell B. A., Kersting A. B., Zavarin M., and Zhao P. "Development of a Composite Non-Electrostatic Surface Complexation Model Describing Plutonium Sorption to Aluminosilicates" Lawrence Livermore National Laboratory, LLNL-TR-408276, 2008.
- Powell, B.A., Zurong Dai, Mavrik Zavarin, Pihong Zhao, Annie B. Kersting. (2011) Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces, *ES&T* 45 (7), pp 2698-2703
- Rusin P. A., Quintana L., Brainard J. R., Strietelmeier B. A., Tait C. D., Ekberg S. A., Palmer P. D., Newton T. W., and Clark D. L. (1994) Solubilization of Plutonium Hydrous Oxide by Iron-Reducing Bacteria. *Environmental Science & Technology* 28(9), 1686-1690.
- Soderholm, L., Almond P.M., Skanthakumar S., Wilson, R.R., and Burns, P.C. (2008) The structure of the plutonium oxide nanocluster *Angewandte Chemie-International Edition* 47(2), 298-302.
- Tien N.C. and Jen C.P. (2007) Analytical modeling for colloid-facilitated transport of N-member radionuclide chains in the fractured rock. *Nuclear Science and Techniques* 18(6), 336-343.
- Tinnacher, R. M. and Honeyman, B. D., 2007. A new method to radiolabel natural organic matter by chemical reduction with tritiated sodium borohydride. *Environmental Science and Technology* 41, 6776-6782
- U.S. Dept. Energy, (2007) Basic research needs for geosciences; facilitating 21st century energy systems. Report from the workshop Feb. 21-23, 2007, pp. 186
- Zavarin, M., B. A. Powell, M. Bourbin, P. Zhao, and A. B. Kersting (submitted), Np(V) and Pu(V) Sorption to Montmorillonite as a Function of Ionic Strength, pH, and Time, *Environ. Sci. Tech.*
- Zika, R. G., J. W. Moffett, R. G. Petasne, W. J. Cooper, and E. S. Saltzman (1985), Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters, *Geochemica et Cosmochimica Acta*, 49, 1173-1184.
- Zimmerman, T. N. "Plutonium humic acid stability constant determination and subsequent studies examining sorption in the ternary Pu(IV)-humic acid-gibbsite system" M.S. Thesis, Clemson University, 2010.

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